VOLUME XIII NUMBER 1

THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED BY

EDWARD L. NICHOLS

ERNEST MERRITT, and FREDERICK BEDELL

LXV

JULY 1901

TABLE OF CONTENTS

Frontispiece

The Effect of Gravity and Pressure on Electrolytic Action — ROLLA B. RAMSEY — 1

On a Newly Discovered Phenomenon Produced by Stationary Sound-Waves — BERGEN DAVIS — 31

On the Heat Evolved when Liquids are Brought in Contact with Powders — C. E. LINEBARGER — 43

On the Density of Ice — E. T. BARNES — 55

Note: Henry Augustus Rowland — 60

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LANCASTER, PA., AND NEW YORK

LONDON: MACMILLAN AND CO., LTD

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Two volumes of THE PHYSICAL REVIEW are published annually, these volumes beginning in July and January, respectively, and containing at least five numbers each. The price of subscription is two dollars and fifty cents a volume (five dollars a year), or fifty cents a number. Subscriptions should be sent to the publishers. THE MACMILLAN COMPANY, 41 *North Queen Street, Lancaster, Pa.*, or 66 *Fifth Avenue, New York;* Messrs. MACMILLAN & CO., LTD., *London;* or to Messrs. MAYER AND MUELLER, *Berlin.*

Previous to Volume V. (July–December, 1897) THE PHYSICAL REVIEW was published in annual volumes, each containing six bi-monthly numbers, beginning with the July–August number, 1893. These may be obtained from the publishers at the former subscription price, three dollars per volume.

Subscribers who desire to have their copies of the REVIEW sent to them with the edges cut, can so obtain them by informing the publishers to that effect.

Correspondence relating to contributions should be addressed to the editors, at *Ithaca, New York.*

Manuscript intended for publication in THE PHYSICAL REVIEW must be communicated by the author; when publication in other journals is contemplated, notice to that effect should be given.

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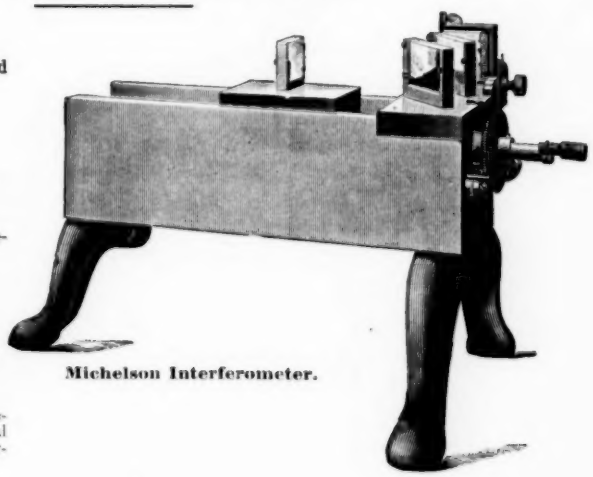

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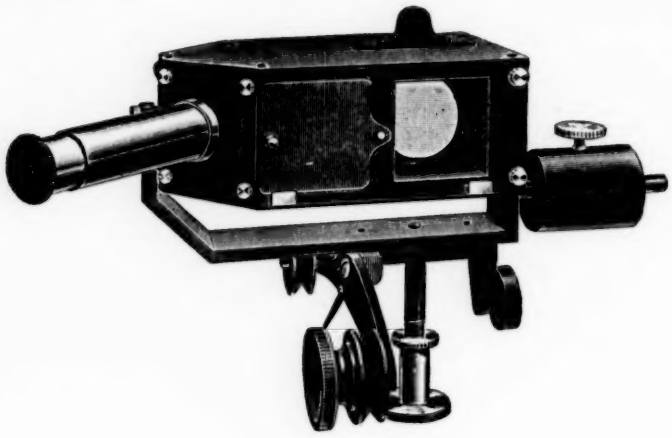

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Volume XIII. *July, 1901.* *Number 1.*

THE

PHYSICAL REVIEW.

THE EFFECT OF GRAVITY AND PRESSURE ON ELECTROLYTIC ACTION.

By Rolla R. Ramsey.

WHEN a current of electricity is passed through an electrolytic cell the anode is dissolved while the cathode is plated. If the cell is made in the form of a tube, with the electrodes in the ends, so mounted as to rotate from a horizontal to a vertical position about a horizontal axis, the law of conservation of energy would lead us to expect a greater consumption of energy in the case in which the current passes up through the tube than when the tube is rotated 90° making the flow along a horizontal plane. The difference in the two cases of the amount of energy consumed in a unit of time will be

$$m\,g\,h,$$

where m is the mass of metal transferred in unit of time, g the force of gravity, h the distance between the electrodes.

If the current strength is kept a constant value of 1 C.G.S. unit, the difference of the potential differences of the two ends in the two cases is

$$E = mgh,$$

where m is 10 times the electro-chemical equivalent of the cation. The above equation can also be put in the form

$$E = \text{Kat}\ gqh,$$

where Kat is the equivalent weight of the cation and q is 10 times

the electro-chemical equivalent of hydrogen. Since, as was first shown by Hittorf,[1] when the cations move with the current the anions move in the opposite direction with a certain definite velocity, the velocity ratios being expressed by the migration constant, n: we have,

$$E = [\text{Kat}\ (1 - n) - n\ \text{An}]gqh,$$

or

$$E = [\text{Kat} - N(\text{Kat} - \text{An})]gqh,$$

where An is the equivalent weight of the anion.

Since E can be regarded as a counter E.M.F. a small current should be detected by short-circuiting the voltameter through a delicate galvanometer.

HISTORICAL.

The Effect of Gravity.—To Maxwell belongs the honor of having first shown that such an electro-motive force should exist.[2] In 1878 Maxwell communicated to Nature,[3] a letter written to himself by F. J. Pirani, in which Pirani stated that he had detected such an electro-motive force. In an added note Maxwell spoke of his own attempt to repeat the experiment but found that the greater part of the deflection, if not all, was due to an air bubble floating up and striking the upper electrode. Pirani found as did Maxwell that the electro-motive force persists after the tube had been placed in the horizontal position. In the same volume of Nature,[4] R. Colley, of Moscow, pointed out that he had published results,[5] which established the fact that such an E.M.F. exists and that he had also calculated its magnitude and verified his results experimentally.

Colley, in his successful method, used a glass tube with the electrodes fused through the walls near the ends. One end of the tube was fused shut while the other had a rubber tube placed over it so as to be closed by means of a pinchcock. Two

[1] Pogg. Ann., Vol. 98, p. 5, 1856.

[2] Maxwell, Vol. I., p. 317, 1st edition.

[3] Nature, Vol. 17, p. 180.

[4] Nature, Vol. 17, p. 282.

[5] Jour. Phy. Chem. of St. Petersb., 1876; Pogg. Ann., 157, pp. 370, and 628, 1876; Phil. Mag., s. 5, Vol. I., p. 419.

such tubes were used in the experiment. The electrodes in one case were of silver and the electrolyte was silver nitrate; in the other they were of cadmium and the electrolyte was cadmium iodide. Wires connected to the electrodes led the current through a resistance box and a sensitive galvanometer, the sensibility of the galvanometer being 8×10^{-9} with a period of 80 sec. He pointed out that it is necessary to remove all air from the electrolyte by means of an air pump. He found by calculation and also by experiment that in the case of silver nitrate the E.M.F. is down, while with cadmium iodide it is up through the tube. The following table contains his results.

TABLE I.

Tube.	Length.	Resistance.	Deflection.	
			Calculated.	Observed.
300 to 381 grams $AgNO_3$ per liter.				
No. I	160 cm.	774 Siemens	8.32	4.3
No. II	360 "	1500 (?) "	16.22	6.9
Saturated Solution CdI_2				
No. II	360 cm.	7976	21.55	6.8

He explained the discrepancy by a statement of Helmholtz, that Ohm's law seems to be inapplicable to weak currents, or that they behave as if the cell had a much larger resistance than calculated. He determined the resistance of the cell by Ohm's method and finds it to be 18240. Using this resistance the calculated deflection was 6.61 compared with 6.83 by experiment.

Gore has done considerable work which has more or less bearing upon this subject. In an article entitled Relation of Volta Electro-Motive Force to Pressure,[1] he described a long series of experiments with glass tubes 3 meters long and 1 cm. bore, fitted with paraffined corks through which wires passed for electrodes. The tubes were filled with the electrolyte through a T at the middle leaving an air bubble of .5 cm. In some cases as many as five of these tubes were mounted side by side and connected in series, the lower end of one being connected to the top of the next. These were connected through a galvanometer and a resistance of 50,000

[1] Phil. Mag., Vol. 35, p. 97, 1893.

ohms. The method of procedure was to place the tubes in a horizontal position until the galvanometer came to a steady position and then to turn the tubes to the vertical position and note the maximum deflection which was obtained in from 4 to 10 minutes. He says, "No perceptible amount of interference was caused by the small difference of temperature between the top and the bottom of the room usually equal to about 1°.5 C." The electrodes were made from the same piece of metal. The electrolytes were solutions of various salts of varying proportions. The results are given in terms of galvanometer deflection, the sensibility not being given except in one case. (Expt. 93, 8° corresponds to an E.M.F. of .00572 volt.) Experiment 93 was with zinc electrodes in an electrolyte of KCl. Two tubes were in series making $h = 600$ cm., which will give approximately 1×10^{-5} volts per cm. height (compared with 2.4×10^{-8} volts for zinc in $ZnSO_4$). Of 91 experiments, 41 showed a perceptible current. Of the 41, 39 were up. With zinc in zinc sulphate he detects no current. Dr. Gore also tried the effect of pressure by making a tube with a porous biscuit-ware diaphragm inserted between the electrodes. By means of this and a tube fused into the first he was able to keep both electrodes at atmospheric pressure while their difference in height was 3 meters. Upon connecting to the galvanometer he was unable to detect a current. He next placed both electrodes in the same horizontal plane with the diaphragm inserted between them and by means of a rubber tube filled with mercury he was able to vary the pressure on one while the other was at atmospheric pressure. A pressure of 30 inches of mercury gave a deflection of 6° and a pressure of 52 inches gave 12°. The electrode which was under pressure was positive to the other.

Dr. Gore's second article is interesting on account of its errors rather than results. The article is entitled Influence of Proximity of Substance upon Voltaic Action.[1] In his experiments he made use of 72 pigs of lead, weighing 8,271 lbs., as an influencing mass. From his calculation he shows the looked-for effect to be $1/24 \times 10^{-8}$ of the effect due to the force of gravity. (Which would be 1×10^{-17} in the case of zinc in zinc sulphate solution.

[1] Phil. Mag., Vol. 43, p. 440, 1897.

With potassium chloride the effect will be even less since the equivalent weights of the ions are nearly equal and the migration constant, $n = .516$.) The apparatus used was a number of cells in series mounted so as to rotate in a horizontal plane about a vertical axis, thus presenting either end to the mass of lead. Dr. Gore says there were several disturbances but they were sufficiently small to permit a very minute deflection of the galvanometer due to the presence of the lead provided a proper method of averaging the magnitudes was employed. The second apparatus consisted of a number of tubes in series mounted so as to slide endwise into and out of lead tubes, one end entering as the other receded. The third apparatus was built on the same general plan with the tubes of larger cross section, thus reducing the resistance. He concludes from his results that the proximity of lead increases the positive condition of the electrodes. A galvanometer was used in this experiment; probably the one used in the first experiment. Judging from the calculated values and the sensibility of the galvanometer, we are pretty safe in saying that the effect detected by Dr. Gore was not due to the gravitational attraction of the lead on the ions.

In an article entitled Unpolarizable Electric Cells under the Influence of Centrifugal Force, Th. Des Coudres[1] gives results obtained with two cadmium voltameters mounted as to be rotated about a vertical axis. The tubes were each 20 cm. long so placed that the electrodes were approximately 10 and 20 cm. from the axis of rotation. The electrolyte was a solution of cadmium iodide. This salt is especially suited to show the gravitational effect on the ions, since the equivalent weight of cadmium is 56 and that of iodine is 126, while the migration constant is greater than 1. In the solution used by Des Coudres it was 1.12. The results are given in terms of revolutions per sec.

TABLE II.

1 Part CdI_2 to 3.6 H_2O.			
E.M.F.	155.	75.3	37.4 micro volts.
Revs. obs.	5.8	3.87	2.9 per sec.
" Calc.	5.2	3.7	2.6 " "

[1] Wied. Ann., Vol. 49, 254, 1893.

It is to be noted that the value given for the E.M.F., as is pointed out by Des Coudres in a later article, should be divided by two since the values used for the equivalent weights are twice too large.

Des Coudres has also measured the direct effect of gravitation on the ions.[1] In this work he uses a glass tube with cadmium amalgam electrodes; the tube being mounted so as to revolve about a horizontal axis. The method of measurement was by means of a potentiometer which gave the result in terms of a Daniell cell. Connection from the voltameter to the galvanometer was made by means of glass and rubber tubing filled with mercury. The reversing key was a four-way glass stopcock. A detailed discussion is given of the various corrections which enter into the result. First, the correction for the buoyant force of the electrolyte; second, a small E.M.F. due to concentration caused by compression; third, the compression changes the density of the salt in solution making a correction to the first correction; fourth, a concentration change due to diffusion; fifth, a thermal E.M.F. due to heat liberated by compression. He shows that all these corrections except the first are so small as to be neglected without impairing the observed results. The results are given in terms of the migration constant. He finds that for a 23.8% solution of cadmium iodide $n = 1.236$; Hittorf's[2] result being 1.184, that of Lenz[3] 1.165 to 1.161.

Des Coudres then discarded cadmium iodide and used more simply constituted electrolytes. A voltameter was built of two tubes of such form as to be kept in water-baths. These baths were suspended from pulleys over head in such a manner as to raise one while the other is lowered through a distance of 4 meters. The two glass tubes were connected by a rubber tube filled with the electrolyte. The electrodes were made of mercury.

His results are given in the following table. They are calculated from the mean of from four to eleven determinations of a particular resistance, w_3 on the potentiometer.

[1] Wied. Ann., Vol. 57, p. 232, 1896.
[2] Pogg. Ann., Vol. 106, p. 543, 1859.
[3] Mem. Acc. Petersb. (9), Vol. 30, p. 36, 1882.

TABLE III.

Salt.	NaCl	BaCl	LiCl	KCl	HCl	$CdCl_2$	
						Cal. El	Amalg. E
Sol. %	19.9	17.	17.3	16.8	3.56	30.1	30.1
E	−0.315	+11.7	−1.09	+10.51	− .218	−1.83	−2.21
n Calc.	.66	.64	.77	.50	.150	1.10	1.02
n Obs.	.65	.65	.75	.52	.175	.82	.82

THE EFFECT OF PRESSURE.

H. Wild[1] has done some work upon the change of E.M.F. between metal and fluids. He concluded that the E.M.F. between amalgamated zinc and zinc sulphate by increasing the pressure two-thirds of an atmosphere does not change by an amount of 1/40000 of a Daniell. Bichat and Blondlot[2] have detected a slight increase of E.M.F. when platinum copper and platinum silver couples immersed in electrolytes were subjected to pressure.

The variation of E.M.F. of various forms of cells with pressure has likewise been studied by Henri Gilbault.[3] The method used was to make a small cell in a test-tube which was placed in a piesometer filled with oil. Pressure was applied by means of a Ducretet pump. Variations of the E.M.F. were measured by the potentiometer method, method of opposition, and a reverse potentiometer method in which the auxiliary cell had a lower E.M.F. than the cell investigated. A Lippmann electrometer was used to indicate the points of perfect balance. Gilbault has shown that the variation of the E.M.F. with pressure in non-polarizing cells may be expressed by the equation:

$$E_p - E_0 = Pdv.$$

Where P is the pressure expressed in dynes and dv is the change in volume of the contents of the cell when 1 C.G.S. unit of quantity has passed through the cell. His results are as follows:

[1] Pogg. Ann., Vol. 125, p. 119, 1865.
[2] J. de Phys. (2), Vol. 2, p. 503, 1883.
[3] Lum. El., Vol. 42, pp. 7, 63, 175, 220, 1891; C. R., Vol. 113, p. 465, 1891, and Electrician, Vol. 27, p. 711, 1891.

TABLE IV.

Pressure = 100 Atmospheres.			
Cell.	Per cent. Solution.	Obs.	Calc.
Daniell.	13 % $ZnSO_4$	6.6	7.18 $\times 10^{-4}$ volts.
"	20 % "	5.0	5.17
"	27.56 "	2.2	2.00
Warren de la Rue.	1 % $ZnCl_2$	13.	13.24
"	40 % "	−5.	−5.04
Lalande.		−10.	−13.5
Planté Accumulator.	8.8 H_2SO_4	−12.	−12.7
"	9.5 "	−5.	−4.95
Volta.		−600.	−586.
Bunsen.		−405.	−383.
Gas battery.		845.	865.

This survey of the work done upon the effects of gravity and pressure shows that the looked-for effect in the case of gravity has been obtained with considerable degree of accuracy by using the chlorides of the metallic earths and with a much less degree of accuracy by using cadmium iodide; while the effect of pressure on the more common forms of commercial cells gives results which accord with theory in a very remarkable manner.

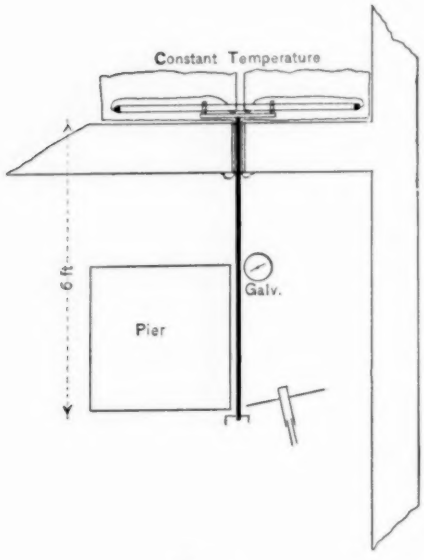

Fig. 1.

Effect of Gravity.

Apparatus and Methods.— The work about to be described has been done with zinc and cadmium sulphates, the two most important electrolytes perhaps used by the physicist. The voltameter was mounted so as to rotate end over end about a horizontal axis in the constant temperature room of the Physical Laboratory. This room is a small inside room surrounded with brick walls and

closed with double doors. The voltameter was turned by means of a brass rod, which served as the axis of rotation, and which passed through a small hole in the wall into the observation room where it extended past and was supported by a brick pier (Fig. 1). The length of this rod was about six feet. The pier, which extended to the second floor, also served as a support for a bracket to which the galvanometer was suspended. The galvanometer used had a resistance of 733 ohms and was capable of giving a sensibility of 2×10^{-10} with a period of 18 sec. The connecting wires were insulated copper, all connections being made with binding posts, mercury or solder. To guard against the possible contact of the wires by the rotation of the voltameter one of the wires leading from the cell passed through a rubber tube. Mercury reverse and break keys were inserted so as to reverse the current and to cut the voltameter out of the galvanometer circuit while finding the sensibility.

Voltameter No. I. (Fig. 2) was constructed of two small bell-jars

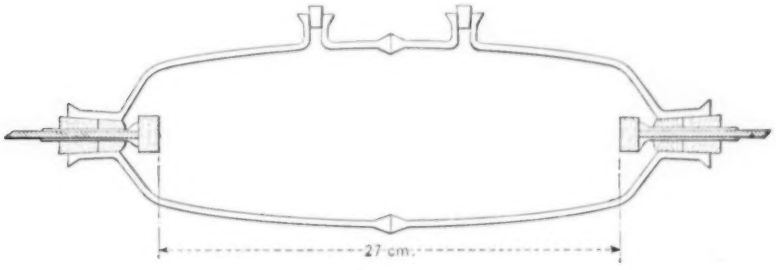

Fig. 2.

with openings in the top and sides. These were cemented together with bicycle cement after having electrodes fixed in the ends by means of corks and cement. The electrodes were cast from C. P. zinc. When constructed the distance between electrodes was 27 cm., the diameter 7.5 cm. The electrolyte was a 10-per-cent. solution of zinc sulphate (10 grams of salt dissolved in 90 cc. water). The method first used was to place the cell in one arm of a wheatstone bridge and to balance it against an equal resistance and observe the deflection of the galvanometer when the voltameter was reversed. From the figure of merit of the galvanometer, the average difference of deflection in the two cases, the resistance of the

various arms, and the E.M.F. of the battery the counter E.M.F. in the voltameter was calculated using Kirchhoff's laws. By this method the counter E.M.F., *i. e.*, the E.M.F. due to gravity, was found to be down through the voltameter. In 1898 the mean of 1,350 readings taken by this method showed the E.M.F. down to be 4.48×10^{-4} volts. This was with a voltameter diameter of which was 4 cm. and length of which between electrodes was 9 cm. A possible explanation of this deviation from the results found later is the polarization of the electrodes due to the large current and the friction of eddy currents in the electrolyte caused by the rotation of the voltameter. As this method promised very little the voltameter was short-circuited through the galvanometer and a resistance box. Upon rotating the voltameter a throw of the galvanometer needle was observed. In every case the throw indicated a momentary E.M.F. opposing the constant E.M.F. This momentary E.M.F. was large enough to give a throw of 20 mm. when the E.M.F. per scale diversion of the galvanometer was 1.3×10^{-4} volts. The constant E.M.F. referred to above is always present and of considerable magnitude in voltameters with metal electrodes. With amalgam electrodes it is considerably smaller and at times almost nil. It is caused, no doubt, by the small differences in the chemical and physical properties of the two electrodes and of the electrolyte surrounding the two electrodes.

To prevent the free circulation of the electrolyte in the voltameter, which was thought to be the cause of the disturbance in No. I., voltameter No. II. was built. (Fig. 3.) This was made from

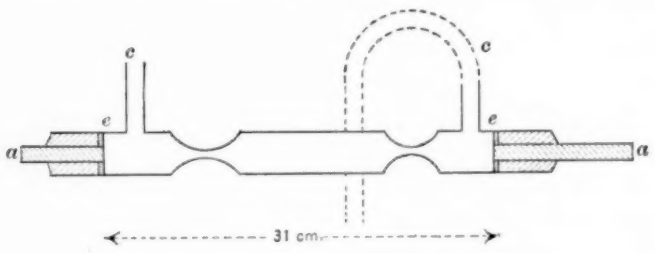

Fig. 3.

glass tubing 1–½ cm. diameter. The length between the electrodes was 31 cm. A short distance from the electrodes the tube was

drawn down to small diameter. T tubes were fused in the ends near the electrodes for convenience in filling. The electrodes, *a*, were made of a bar of C. P. zinc cut in two in the middle; the two contiguous parts being exposed to the electrolyte. These were fastened in the tube by means of short perforated corks, *c*, and a filling back of the corks of melted cement. This tube was provided with the proper mountings and placed on the end of the brass shaft after being filled with the electrolyte. To exclude air bubbles the tubes, *c*, were closed carefully with ordinary corks. This tube also gave a throw when rotated from horizontal position to vertical, or from the vertical position through 180° to vertical. When rotated from horizontal through 180° to horizontal no deflection was detected. Short-circuiting the voltameter by a wire connecting the two electrodes together removed the disturbance, showing that it was in the tube and not due to magnetic influence. To try the effect of pressure on the electrodes without changing their position, a U tube was fused to one of the tubes, *c*, while the other was fused shut. Pressure was applied by placing over the U a rubber tube filled with mercury. This tube passed through

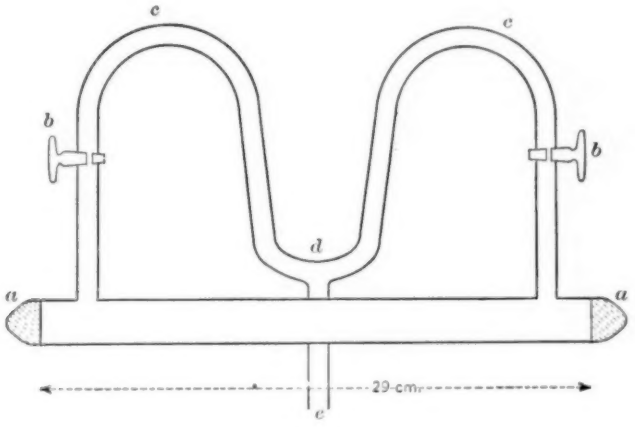

Fig. 4.

the wall along a shelf and was connected to a reservoir which could be raised and lowered by the observer at the telescope. The galvanometer gave a throw in the same direction both when putting on and relieving the pressure. The variation of pressure was approxi-

mately from zero to two atmospheres. The momentary E.M.F. opposed the E.M.F. of the voltameter.

To more fully investigate the cause of the pressure disturbance tube No. III. was built (Fig. 4). This tube was made by taking two pieces of glass tubing and fusing a platinum wire in one end of each. T's were also fused into these a short distance from the ends. To these T's long narrow tubing with glass stopcocks were fastened. In the end containing the platinum wire zinc amalgam was placed. After this operation the two tubes were fused together making an enclosure which would be absolutely rigid except for the elasticity of the glass. The smaller tubes were bent in the form of a U above the stopcocks and joined to a T by means of rubber tubing. After the voltameter had been filled with the electrolyte up to the bend in the side tubes and the rubber tube, filled with mercury, had been attached to the T tubes, *e*, the pressure could be varied at will by raising or lowering the reservoir of mercury in the observation room. By means of the stopcocks the pressure could be applied through one or both ends. By this means the slight flow of the electrolyte due to the expansion of the glass due to pressure could be made to wash either electrode. The effect of variation of pressure on this voltameter was not very marked. By a careful comparison of a large number of observations a slight increase of current is noted when the pressure is increased. This effect can be explained to some extent at least by the decrease of resistance due to pressure. Upon relieving the pressure the effect is not so marked, if present at all. From these results it would seem that the effect noted in voltameter No. I. and No. II. was due to the kind of electrodes and the manner of inserting them in the tube. Since the cement used was of about the consistency of Burgundy pitch the added pressure would move the electrodes to a certain extent. To obviate the pressure due to the electrolyte, a voltameter (Fig. 5) was constructed in which zinc sulphate paste was used as an electrolyte. This tube was made in the form of an H, the zinc amalgam electrodes being placed in the diagonally opposite ends of the arms. The zinc sulphate paste was made by grinding zinc sulphate and water together in a mortar until it was a semi-fluid. This was placed in the tube and the ends of the arms

opposite to the electrodes were closed with corks over which melted bicycle cement was placed. On account of the great difference in the electrolyte immediately next to the electrodes a comparatively high E.M.F. was always present. This required a high

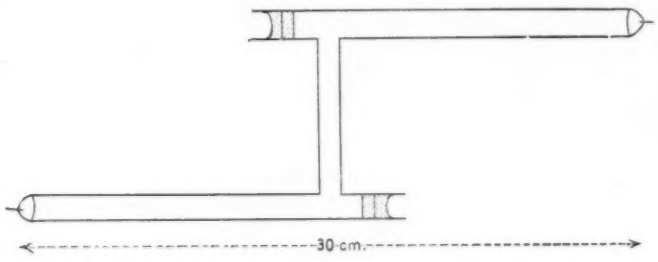

Fig. 5.

resistance to keep the deflection of the galvanometer on the scale. This resistance cut down the sensibility to such an extent that readings were impossible.

During these experiments the disturbing elements due to the Dynamo Laboratory, and to varying currents in the neighboring power and car lines rendered the reading very uncertain and at times impossible. To better the conditions observations were made between 11 P. M. and 6 A. M. It was found that after midnight the disturbances were approximately one-tenth of those in the daytime. Never in any case was it possible to read the deflection to within 1 mm. with any degree of accuracy when the galvanometer was in its most sensitive position. Finally after wasting several nights the method of multiplication was tried. In this method the E.M.F. of the circuit is reversed in unison with the swing of the galvanometer needle until a final maximum deflection is reached, the maximum depending upon the E.M.F. and the damping factor of the galvanometer.

Let A_0 be the deflection of galvanometer.

" A_1 " " " " first swing.

" A_2 " " " " second swing.

" A_n " " " " nth swing.

In case of no damping

$$A_1 = 2A_0.$$

With damping,

$$A_1 = A_0 + A_0 e^{-\lambda} = A_0(1 + q) \qquad \text{where} \qquad q = e^{-\lambda}$$

$$A_2 = A_0 + A_1 q + A_0 q = A_0(1 + q)(1 + q)$$

$$A_3 = A_0 + A_2 q + A_0 q = A_0(1 + q)(1 + q + q^2)$$

$$A_4 = A_0(1 + q)(1 + q + q^2 + q^3)$$

$$A_n = A_0(1 + q)(1 + q + q^2 + q^3 + \ldots + q^{n-1})$$

$$A_n = A_0\left(\frac{1 + q}{1 - q}\right)$$

$$A_0 = A_n\left(\frac{1 - q}{1 + q}\right) = A_n\left(\frac{1 - e^{-\lambda}}{1 + e^{-\lambda}}\right).$$

The damping factor was computed from the observed value of the logarithmic decrement λ but it was found that better determinations could be had by placing a reverse key in the circuit and reversing a known E.M.F. in unison with the swing of the needle. This damping factor varied with the sensibility of the galvanometer. A number of results at different sensibilities were found, and with the results a curve (Fig. 6) was plotted using galvanometer sensibilities as

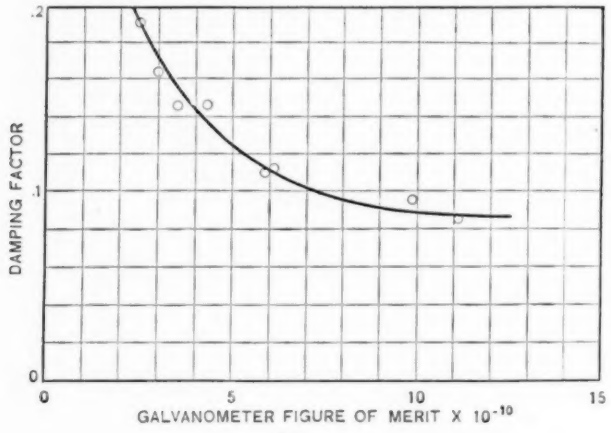

Fig. 6.

abscissas and damping factor as ordinates. The damping factors used in the later calculations are read from the curve.

To use this method in the case of the determination of the E.M.F. due to gravity, we start with the voltameter horizontal and the galvanometer at rest; suddenly turn the voltameter to a vertical position and at the instant the needle reaches its greatest elongation turn the voltameter through 180°, repeating the operation when the needle reaches its greatest elongation on the other side. This process is continued until the deflection reaches a maximum. If the magnetic field changes a larger or smaller deflection will be noted depending upon the position of the needle at the instant, but by rotating in unison with the needle the old maximum will be obtained. The advantages of this method of observation are: large deflections, the elimination of the effect of disturbances in the magnetic field, and the elimination by repeated reversals of the tube of the thermal E.M.F. due to the difference of the temperature of the two ends. The disadvantages are: errors due to not rotating the tube at the proper instant, and errors due to duration of rotation. With proper precautions the errors of this method are very small. The cycle of operations by means of which the results given in the following tables were obtained was as follows:

(*a*) Starting with the tube in normal position (horizontal and commutator *straight*) the tube was turned to the vertical position and reversed repeatedly in unison with the galvanometer needle until a maximum deflection was obtained.

(*b*) The above operations were repeated with the commutator reversed. These operations were followed until six determinations of the maximum deflection was obtained.

(*c*) Starting with the tube horizontal but turned 180° from the normal position, the tube was turned to the vertical and rotated until a maximum deflection was obtained. The commutator was straight and reversed alternately as before until six more determinations were obtained. The mean of the twelve determinations of the maximum deflection was taken.

Table V. contains a set of readings which will illustrate the method.

Voltameter No. V. (Fig. 7) which may be described as a sample of all made afterwards was made of glass tubing the inside diameter of which was about 1 cm. The amalgam electrodes were made by first solidifying the amalgam in the ends of short pieces of

TABLE V.

Dec. 27-5-15-*P.M. Tube No. VIII. Length* 144 *cm. R. of tube* 9,300 *ohms.*
Galv. R = 733 *ohms. Fig. M.* = 1.5×10^{-10}.

Voltameter Normal.					
Commutator Straight.			Commutator Reversed.		
Right End.			Right End.		
Down.	Up.	Difference.	Up.	Down.	Difference.
146	137	9	231	220	11
160	152	8	214	205	9
178	166	12	193	180	13
Voltameter Reversed.					
186	175	11	184	174	10
208	202	6	174	165	9
208	200	8	168	158	10

Mean difference 9.5 mm.
Damping factor .23.
E.M.F. per cm. length of voltameter 2.34×10^{-8} volts.

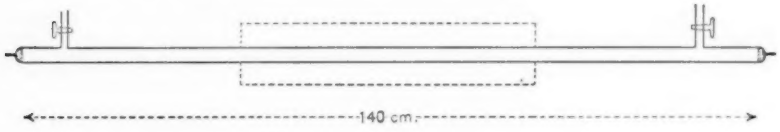

Fig. 7.

tubing and subsequently fusing these to the long tube which formed the body of the voltameter. Side tubes with glass stopcocks were fused on at either end. Some later tubes had only one stopcock the electrolyte being run in through a small capillary tube. The amalgam was made after the formula given by Kahle.[1] This amalgam, however, contained too much mercury to be satisfactory. In order to remove the air bubbles from the electrolyte it was necessary to attach the tube to an air pump. This caused mercury to come to the surface of the electrode and at times to be detached entirely. After letting the pressure of the atmosphere on the electrode, the mercury would disappear from the surface but the metallic lustre between the surface of the glass and the amalgam had disappeared also. This metallic lustre seemed to be an important factor. In every case with zinc amalgam after the electrodes be-

[1] Wied. Ann., Vol. 51, p. 203, 1894.

came granular, disturbances inside the voltameter became so great as to render the tube worthless. The method pursued was to build the tube and place it under the pump, then shake off the extra mercury and allow it to pass out through the stopcock. After this the tube was broken, the amalgam melted and poured out, the short ends with the platinum wire were fused again or new ones made. The amalgam was again placed in the short tubes which were again fused to the longer. To obtain a permanent metallic surface in contact with the inner surface of the glass it was found that it was necessary to place the amalgam in the tube immediately after the latter had been fused. Any moisture in the tubes after being fused gave a poor contact between the amalgam and the glass. Good contact or surface lasted a few days only. In the case of cadmium amalgam, no trouble of this kind was experienced. With amalgam made of 1 part cadmium to 6 parts mercury there was no tendency for mercury to be drawn out when under the pump.

The following table gives the results for 10 per cent. solution of zinc sulphate:

TABLE VI.

Date.	Tube.	Length.	Resistance of tube.	Resistance in box.	Fig. of M.	Damping factor.
Dec. 8.	VI.	143.7 cm.	4353	1000	2.1×10^{-10}	.21
" 11.	VI_b.	144.01	4360	2000	2.08	.21
" 27.	VIII.	144.	9500	0	1.5	.23
" 27.	"	144.	"	0	1.5	.23
" 29.	"	144.	"	0	2.1	.21
Jan. 2.	"	144.	"	1000	3.57	.158

E. per Scale Division.	Max. deflect. An.	A_0	E. obs.	E. per cm. Height.	E. cal.
1.26×10^{-6}	34.5 mm.	7.42	9.36×10^{-6}	-6.5×10^{-8}	-2.4×10^{-8}
1.45	18.5	3.88	5.62	−3.9	
1.54	9.5	2.19	3.37	−2.34	
1.52	12.41	2.86	4.34	−3.02	
2.14	11.16	2.33	5.00	−3.45	
4.05	7.5	1.11	4.5	−3.13	

It will be noted that the values for tube No. VIII., are lower than the values obtained with previous tubes and also that the values obtained with No. VIII. increase as the tube becomes older. Tube

No. VIII. was made with special care to get the electrodes set firmly in the end of the tube. The metallic lustre was perfect when first built, but this passed away with age.

The following is the theoretical calculation of the E.M.F. per cm. height. The value of the migration constant used in this calculation is taken by interpolation from the three values given for zinc sulphate in a table of electro-chemical properties of aqueous solution by Rev. T. C. Fitzpatrick.[1] The value used is $n = .715$ for 10 per cent. solution.

In the formula

$$E = [\text{Kat} - n(\text{Kat} + \text{An})]gqh.$$

we assign for zinc sulphate the following values:

$\text{Kat} = \frac{1}{2}(65) = 32.5$ (equivalent weight of Zn).

$\text{An} = \frac{1}{2}(96) = 48$ (equivalent weight of SO_4).

$g = 980$.

$q = .0001035$ (ten times the electro-chem. equiv. of H).

$h = 1$ cm.

$n = .715$.

The particular solution of E is therefore:

$$E_1 = [32.5 - .715 \times 80.5]\ 980 \times .0001035$$
$$= [32.5 - 57.7]\ .0001013.$$
$$E_1 = -2.53 \text{ C.G.S.}$$
$$E_1 = -2.53 \times 10^{-8} \text{ volts.}$$

From this is to be subtracted the correction for the buoyant force of the liquid, viz.:

$$c = D[\text{Kat } V - nV''(\text{Kat} + \text{An})]gqh:$$

where

D = density of the electrolyte,

V = specific volume of the cathode.

V'' = specific volume of the salt in solution.

putting

$$D = 1.1.$$
$$V = 1/7.$$
$$V'' = 1/10.$$

[1] See Whetham's Solution and Electrolysis, pp. 215–283. B. A. Report 1893.

We have —

$$e = 1.1[32.5/7 - n\ 80.5/10]gqh.$$

$$e = 0.124 \times 10^{-8} \text{ volts.}$$

$$E = E_1 - e.$$

$$E = -2.4 \times 10^{-8} \text{ volts.}$$

The sign — indicates that the current flows up through the tube opposite to gravity. This, perhaps, would seem at first thought to be inconsistent with the law of conservation of energy. It will be noted that when 32.5 grams of zinc is carried with the current that 57.7 grams of SO_4 moves in the opposite direction. The E.M.F. is due to the excess of the mass of SO_4 over the mass of zinc. This E.M.F. will continue until the E.M.F. due to difference in concentration is large enough to balance it. In case the rate of diffusion is great enough to prevent an appreciable difference in concentration the source of energy must be the heat absorbed by diffusion.

With cadmium sulphate the results are a great deal more consistent than with zinc sulphate. The voltameters were made after the same plan as in the case of zinc. The cadmium amalgam was made after the formulæ given by Jaeger & Wachmuth.[1] Although the amalgam became crystalline at the surface of the glass in a short time there seemed to be no tendency for the electrolyte to creep between the two as in the case of zinc amalgam. A difference was noticed between zinc and cadmium amalgam in that the zinc seemed to adhere better to the platinum wire. After melting and pouring the amalgam out of the tube, a coating of the zinc amalgam adhered to the wire while the cadmium amalgam left the wire perfectly clean. While removing the air from the cadmium sulphate solution small bubbles would form constantly. The vacuum was perfect enough to give a metallic click when the electrolyte was shaken. This action seemed to indicate that there might be a slow chemical reaction taking place in the electrolyte.

The results for 10% cadmium sulphate are given in the following table.

[1] Wied. Ann., Vol. 59, p. 575, 1896.

TABLE VII.

Date.	Tube.	Length.	Resistance of tube.	Resistance in box.	Fig. of m.	Damp. Factor.
Jan. 3	Cd No. I	128 cm.	11240	0	4.8×10^{-10}	.127
" 7	"	"	"	0	3.3	.163
" 16	" II	130 cm.	11300	0	3.06	.17
" 19	"	"	"	0	2.27	.202

E. per Scale Division.	Max. deflect. A_n	A_0	E_h	E per cm. Height.
5.82×10^{-6}	2.5	.317	1.85×10^{-6}	-1.44×10^{-6}
3.96	3.51	.556	2.20	−1.72
3.68	4.	.680	2.51	−1.92
2.76	4.5	.910	2.51	−1.92
				Mean −1.75

The migration constant for cadmium sulphate seens never to have been experimentally determined. The constant corresponding to any E.M.F. may however be determined from the equation,

$E = \{[\text{Kat} - n(\text{Kat} + \text{An})] - D\,[\text{Kat}\,V - nV'(\text{Kat} + \text{An})]\}\,gqh$,

where the following values are substituted,

$\text{Kat} = 55.7$

$\text{An} = 48.$

$D = 1.08$

$V = 1/9.39$

$V' = 1/8.4.$

We have:

$$E = 5.02 - 9.17\,n \times 10^{-8} \text{ volts.}$$

Solving from n we have:

$$n = (E + 5.02)/9.17.$$

For

$$E = -1.75 + n = .738.$$

With a nearly saturated solution of cadmium sulphate the E.M.F. is positive or the current flows down through the tube. The following table gives the results for a 46% solution (46 grams of $CdSO_4$ crystals dissolved in 56 grams of water).

TABLE VIII.

Date.	Tube.	Length.	Resistance of tube.	Resistance in box.	Fig. m.	Damp. Factor.
Jan. 29.	Cd No. 11.	130 cm.	7560	1000	6.04×10^{-10}	.11
" 29.	"	"	"	0	4.3	.138
" 29.	"	"	"	10000	4.28	.137
Feb. 1.	"	"	"	0	4.74	.127

E. per Scale Division.	Max. deflect. A_n	A_0	E_k	E per cm. Height.
5.48×10^{-6}	9.4 mm.	1.36	7.5×10^{-6}	5.77×10^{-8} volt.
3.47	11.4	1.59	5.5 "	4.25
8.1	5.6	.77	6.25	4.8
3.85	11.	1.40	5.36	4.12
			Mean	4.78

Calculation gives the following equation for E:

$$E_1 = 4.95 - 8.67\, n \times 10^{-8} \text{ volts.}$$

For

$$E = 4.78,\ n = .02.$$

The meaning of the small value of n is that the anions are moving with a very small velocity in the direction opposite to that of the current. The tendency in a concentrated solution would be for both ions to settle to the lower end of the tube and produce a difference in concentration.

In the above work the resistance of the voltameter was determined by taking the galvanometer deflections with various resistances in the box when the voltameter was in the horizontal position, the constant E.M.F. of the voltameter being used as the E.M.F. of the cell. Plotting the reciprocal of deflections as ordinates and resistances as abscissas, the intercept on the x axis will give the resistances of the cell plus the galvanometer resistance. The results obtained in this manner agree with the accepted values. It will be remembered that R. Colley, in the paper cited in an earlier paragraph of this article, found the resistance to be much larger by this method than the usual method of determination.

EFFECT OF PRESSURE.

Apparatus and Methods.—The effect of pressure on various cells was determined by connecting in opposition two cells whose E.M.F. were nearly equal and measuring the variations of the difference of voltage when one was subjected to pressure. In the first method the cell was made, in the H form, of heavy walled glass tubing with small inside diameter. This cell, which was a cadmium one, was made according to the directions given by Jaeger and Wachsmuth.[1] The electrodes were placed with mercurous sulphate paste over the mercury, and cadmium sulphate crystals over the amalgam. One arm of the tube was fused shut, while the other, which was longer, served as an opening through which the cadmium sulphate solution was passed by means of a capillary tube. By patient work and care the H was entirely filled with the liquid. A long capillary tube was then fused to the cell which connected it to the piesometer. (Fig. 8). Pressure was applied by means of a compression pump.

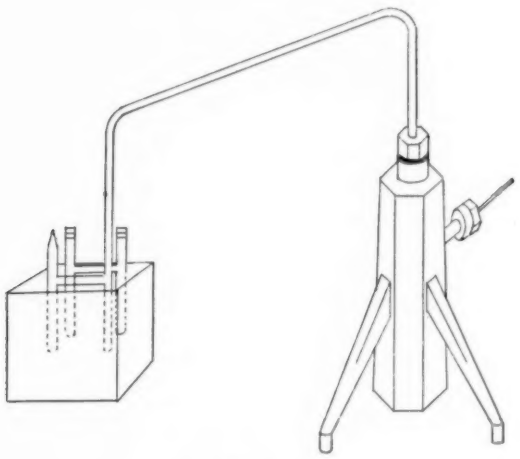

Fig. 8.

The two cells were placed side by side in a block of wood and were connected through a resistance box to the galvanometer. The variation of the E.M.F. was determined by the deflection and sensibility of the galvanometer and the total resistance in the circuit.

[1] Wied. Ann., Vol. 59, p. 575, 1896.

The accompanying curve (Fig. 9) gives the results up to 75 atmospheres at which pressure the connecting tube burst. As the strength of the glass tubing limited the pressure applied, the cells were constructed so as to be placed in a piesometer the inside diameter of which was 2.5 cm. The cells were made in a modified H form (Fig. 10) in which the cross tube was omitted and the vertical

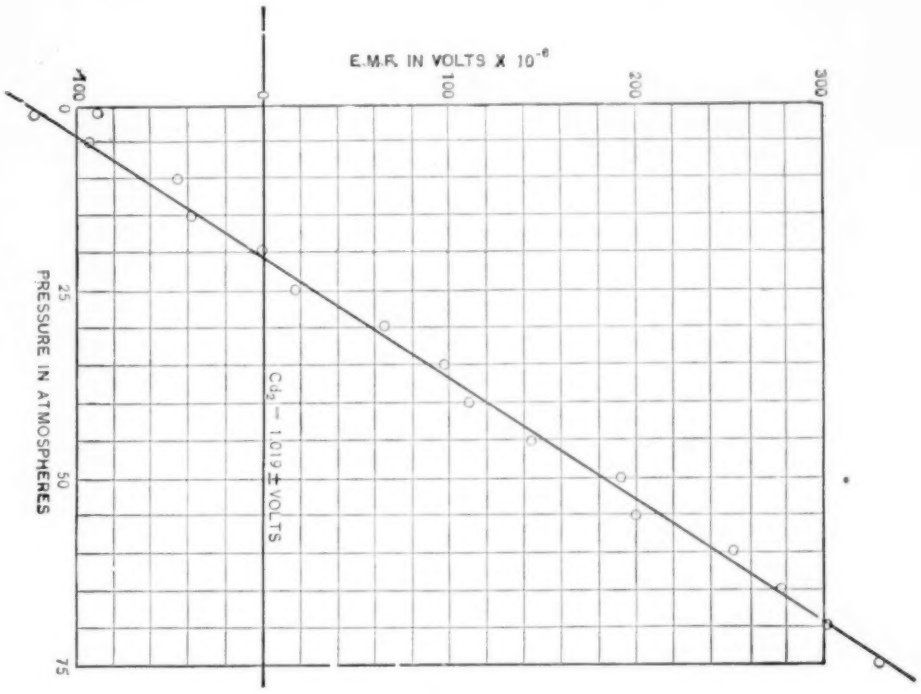

Fig. 9.

ones fused together. This was done by blowing out a small bulb on the side of each tube and then blowing a hole in the bulbs and fusing together at these openings. The electrodes were placed in the ends and the paste and crystals placed over them. Next the cell was heated above the connection and the two tubes drawn down to capillaries. The cell was now filled and the capillaries broken off at the smallest point. It was then placed in the piesometer which was filled with kerosene. By this means the pressure on the inside and outside of the cell will be the same and any possible

solution of the kerosene in the electrolyte will be avoided by the small surface of contact in the capillary tubes. Electric connection was made through two insulated conductors passing through the cap of the piesometer. To avoid errors due to change of temperature the piesometer was immersed in a large water-bath and the compensating cell in a kerosene-bath which was in turn immersed in the water-bath. This water-bath was surrounded with an air-jacket and this with a jacket of sawdust. The covering was made of cotton waste. By this means the temperature of the bath, which was approximately the same as that of the room, could be kept constant during an entire set of observations. Never in any case

Fig. 10.

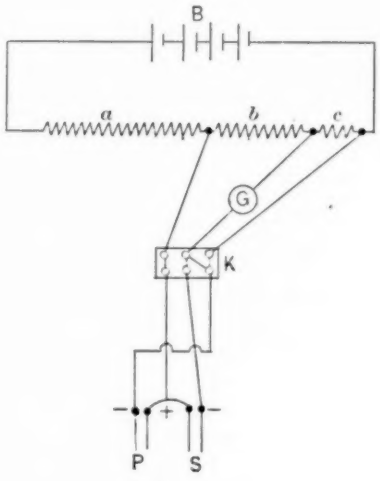

Fig. 11.

could a change be detected by means of a thermometer which was graduated to tenths of a degree.

Instead of determining the change of E.M.F. by means of galvanometer deflections, a potentiometer method was substituted. In this method S (Fig. 11) is the cell under pressure, P is the compensating standard cell, B is the auxiliary battery consisting of four gravity cells, a is a high resistance of from 50,000 to 70,000 ohms; b is a resistance adjusted in proportion to the difference of the E.M.F. of P and S; G is galvanometer; and K is triple mercury key by means of which the cells P and S can be balanced on the poten-

tiometer. The connections as marked by the heavy lines, permit the cell P to be balanced by the resistance b, while the connections as shown by the dotted lines permit the difference of the two cells in case the E.M.F. is less than P, being balanced by c. When the cell under pressure S has a higher E.M.F. than P, the balance can be made on c by diagonally connecting the four right hand mercury cups. The smaller the difference of the E.M.F. of the two cells the less will be the error introduced by any variation of the E.M.F. of the battery B.

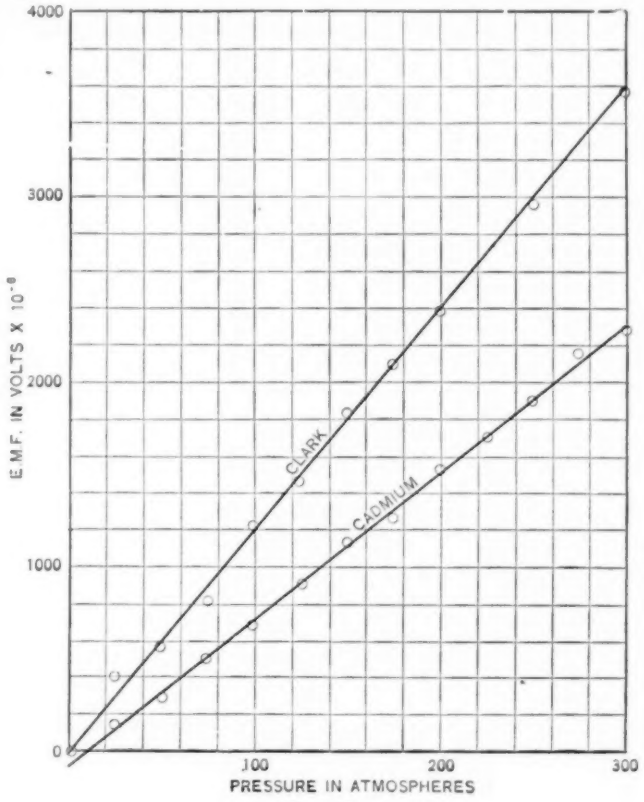

Fig. 12.

By means of this method the change of a cadmium cell with pressure up to 300 atmospheres, was determined. It was found to be linear as is shown by the curve (Fig. 12). In a Clark cell, made according to the directions given by Kahle,[1] the change is linear as

[1] Wied. Ann., 51, p. 203, 1894.

shown by curve (Fig. 12), but it is necessary to allow the cell to stand a few minutes at each pressure in order to allow the E.M.F. to become constant. The time lag is shown by the curve (Fig. 13) in which time is the abscissa and E.M.F. is the ordinate. This may be explained by supposing that the change of E.M.F. at any time is due to the superposition of two changes ; a positive one due to pressure and a negative one due to increase of temperature caused by pressure.

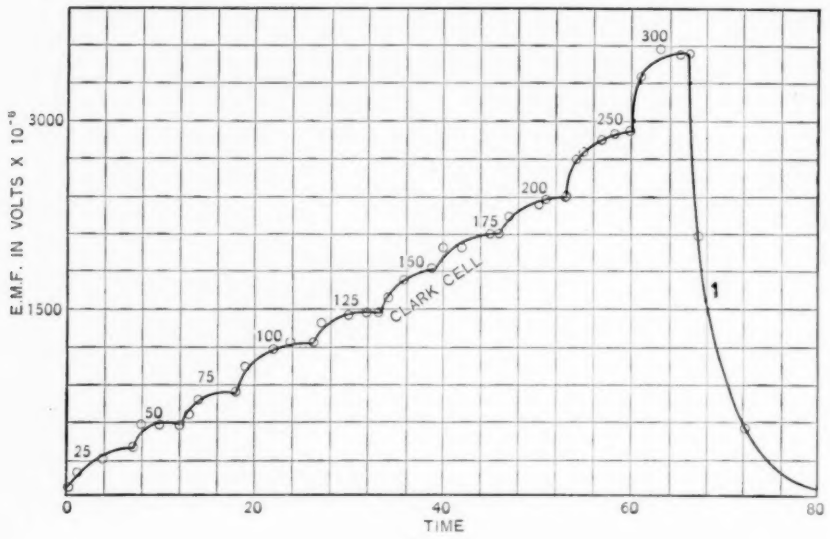

Fig. 13.

After a few minutes the cell regains its original temperature and the increase is that due to pressure alone. In a Carhart Clark cell, made in the H form with zinc amalgam electrodes but otherwise according to the directions given by Carhart,[1] the time lag is more pronounced than in the Clark. The curve (Fig. 14) gives both the time lag and the linear variation of E.M.F. with pressure, since the time intervals are equal. In the one-volt calomel cell, made in the H form but otherwise according to Carhart,[2] the curve (Fig. 15) rises rapidly for the first 25 atmospheres and then bends over, reaching a small linear increment at 100 atmospheres. The satu-

[1] Carhart, Primary Batteries, p. 90.
[2] Am. J. Soc., Vol. 46, p. 60, 1893.

rated calomel, made the same as the zinc calomel, except that the zinc chloride solution is saturated, gives the same kind of curve

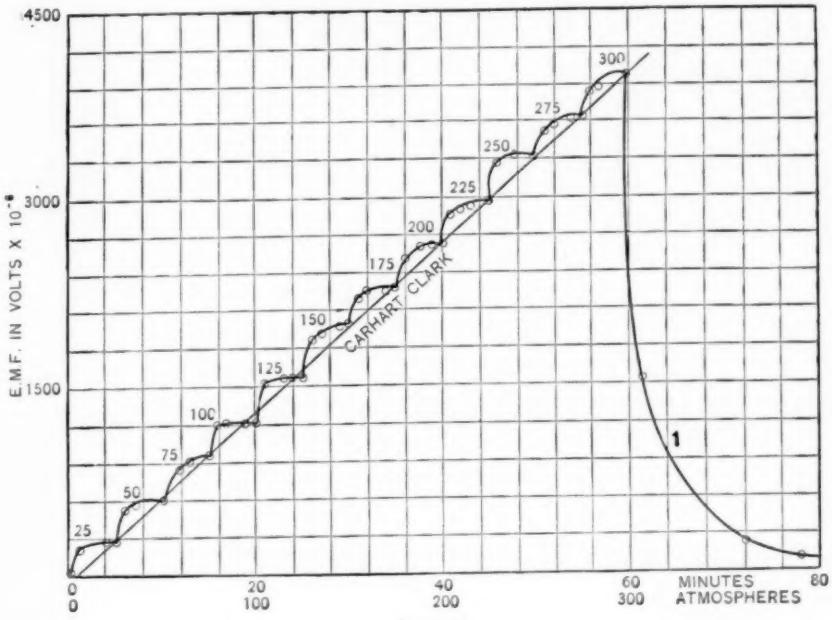

Fig. 14.

(Fig. 15) as the one-volt calomel. The rise at first is not so great and the linear part of the curve is slightly steeper than that of the one-volt calomel. The E.M.F. of this cell was .856 volt. In the

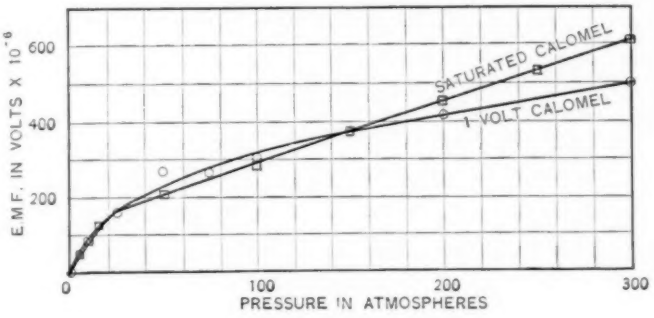

Fig. 15.

copper sulphate cell the variation was quite small and in the negative direction. This cell was made in the H form with zinc amal-

gam and copper, placed on a platinum wire, as electrodes. The zinc amalgam was covered with zinc sulphate paste, and the copper electrode was surrounded with a saturated solution of copper sulphate containing an excess of the crystals. After a diaphragm of blotting paper had been inserted over the copper sulphate solution the cell was filled with a saturated solution of zinc sulphate. The E.M.F. of this cell was 1.078. The time lag was very great, requiring fifteen minutes to settle to a constant value. This rendered the observations slow and uncertain. The silver chloride cell made

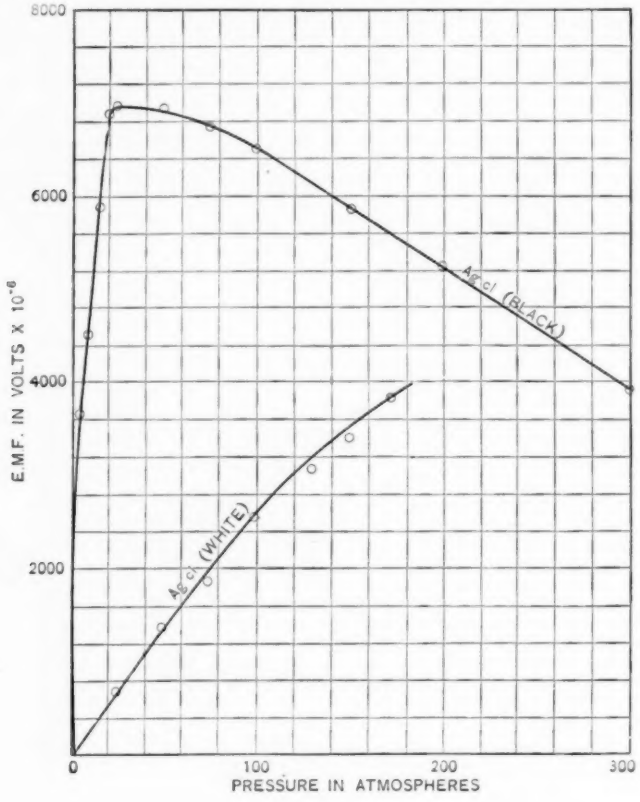

Fig. 16.

according to the directions given by Carhart,[1] except that zinc amalgam was used instead of zinc, gave a curve (Fig. 16) which is nearly linear but curves slightly to the right. The silver chloride

[1] Carhart, Primary Batteries, p. 62.

used in this cell was freshly precipitated from a silver solution, and cast about the silver wire. The same cell with an old silver chloride electrode which had been in the laboratory twenty or more years, and had turned black, gave a very rapid increase of E.M.F. for the first 25 atmospheres and then diminished as shown by the curve marked AgCl (black) (Fig. 16).

A comparison of the pressure effects on the various cells investigated are given by the curves (Fig. 17) and also a tabulation of re-

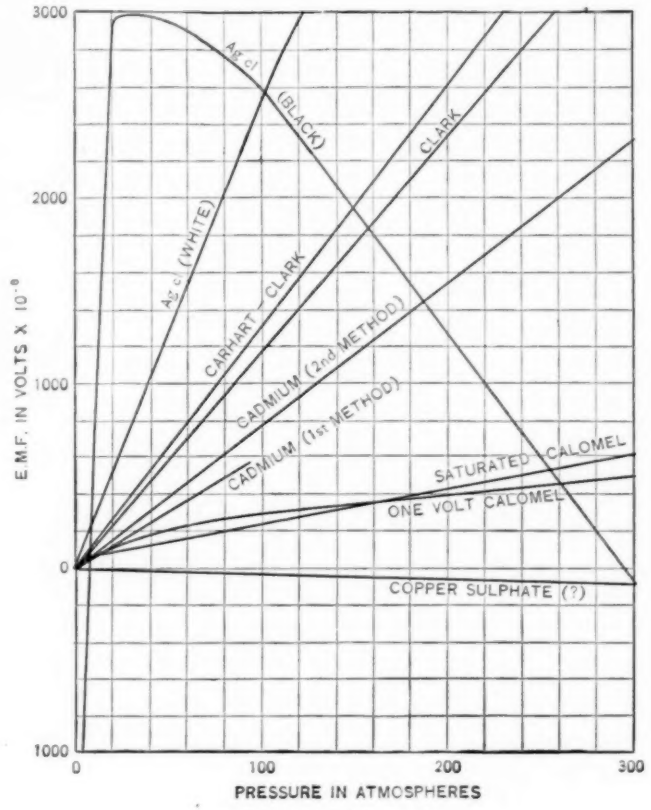

Fig. 17.

sults in Table XI. In Fig. 17 the zero line for the curve AgCl (black) has been dropped to — 4000.

The E.M.F. of the cells were determined by comparison with cadmium and Clark cells, assuming the E.M.F.'s and temperature coefficients as given by the Reichsanstalt.

TABLE XI.

Variation of Pressure given in Volts $\times 10^{-6}$ per Atmos.				
	E.M.F. of Cell.	Temp.	Increase of E.M.F. to .100.	Mean Increase from 100 to 300 Atmos.
Cadmium (1st method).	1.019	20°.4	6.02	
Cadmium (2d method.)	1.019	19°.	7.6	7.6
Clark.	1.440	16°.6	11.6	11.6
Carhart-Clark.	1.443	16°.3	13.1	13.1
One Volt Calomel.	.996	15°.	3.	.98
Saturated "	.805	17°.	2.8	1.63
Copper Sulphate.	1.078	17°.	−1.(?)	−1.(?)
AgCl (white).	1.076	18°.	25.7	15.
AgCl (black).	1.164	15°.6		−13.

This investigation was made under the direction of Professor E. L. Nichols to whom I express my thanks for suggestions made and for the apparatus placed at my disposal.

CORNELL UNIVERSITY, May, 1901.

ON A NEWLY DISCOVERED PHENOMENON PRODUCED BY STATIONARY SOUND-WAVES.

By Bergen Davis.

IN the course of an investigation upon the action of stationary sound-waves, under certain conditions I have observed, that if a small cylinder which is closed at one end, is placed in a stationary sound-wave, it will not only arrange itself perpendicular to the wave, but will also move across it in a direction perpendicular to the stream-lines. The force producing this motion is of considerable magnitude, and it acts normally to the closed end of the cylinder, causing it to move in the direction of the closed end, *i. e.*, the closed end is driven towards the wall of the organ-pipe.

A short description of this phenomenon has already been published,[1] since which a more complete investigation has been in progress.

Description of Apparatus.

The stationary wave used was that obtained in a stopped organ-pipe when blown so as to produce its first overtone. Two nodes were thus obtained, one at the stopped end and the other near the mouth. A thin rubber diaphragm was inserted in the pipe at this node as shown at *d* in Fig. 1. I have found, as has been observed by Lord Rayleigh,[2] that a thin diaphragm at a node does not alter the intensity of the sound appreciably. This diaphragm kept the interior of the pipe free from any disturbances that might arise from blowing.

Two pipes were used in these experiments, a long one and a short one. A section of the longer pipe is shown in Fig. 1. The length of the pipe was 216 cm., from the mouth to the end. It was provided with a movable stop which could be placed at various

[1] Am. Journal of Science, Sept., 1900.
[2] Phil. Mag., Vol. XIV., p. 186, 1882.

positions as *A*, *C*, *I* and *H*. One side of the pipe from the diaphragm to the end was removed and a glass panel substituted for it. This arrangement made the whole of the interior of the pipe visible from the diaphragm to any position of the movable stop. A slit about 8 mm. wide, extending from near the diaphragm to near the end, was cut into the upper side of the pipe. This slit was

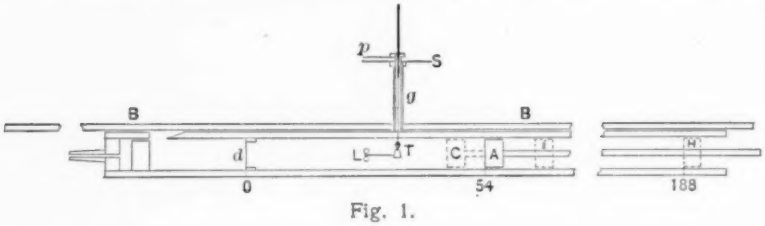

Fig. 1.

covered by a long wooden bar *B* of about 2.5 by 3 cm. in cross-section. The side of the pipe around this slit was lined with kid skin. The bar when pressed down upon this closed the slit and rendered the pipe air-tight. A glass tube *g*, carrying at the top a circular, graduated scale *s*, was inserted in the bar near its center. The torsion wire passed down this tube into the pipe. By this arrangement the torsion balance *T* could be moved along the pipe to any desired position.

The diaphragm was placed at 16 cm. from the lip, as this was found to be the position of the node. A centimeter scale was placed along the pipe, the zero being at the diaphragm, *i. e.*, the first node.

The readings along this scale will also represent distances along the stationary wave. The pipe was 6.7 cm. by 5.5 cm. in cross-section, the height of the mouth opening being 3 cm.

The shorter pipe may also be represented by Fig. 1, by considering the end of the pipe to be at stop *A*, and this stop immovable. This pipe was 67.8 cm. long from lip to stop and 5.3 cm. by 6.4 cm. in cross-section. The height of the mouth opening was 1.8 cm. The arrangements for torsional measurements were the same as those of the longer pipe. The diaphragm was placed at 15.8 cm. from the lip as this was found to be the position of the node.

A mercury manometer was used to regulate and compare the forces of blowing in the various experiments. It consisted of a U

tube of small bore containing mercury, which was inclined at an angle of 30° to the horizontal, so that the total difference in height of the mercury surfaces in the two branches was equal to the reading on a scale placed along one of the branches.

The torsion wire was No. .0035 platinum-silver. Its constant was determined by two methods: By observing the time of vibration of a suspended circular disc of known dimensions and mass; and by connecting the end of the torsion arm to the pointer of a chemical balance, and on turning the torsion head, observing the number of milligram necessary to bring the pointer back to zero.

The two methods gave the same result. The constant was such that a force of one dyne acting at the end of an arm one centimeter in length, attached to a wire one centimeter long produced a deflection of .3° of arc.

The cylinders, the force of whose tendency to move was to be measured, were of four sizes. Three of them were made from gelatine capsules such as are used for medical purposes. The other, the largest one, was made of stiff paper. The dimensions of the cylinders were as follows:

TABLE I.

	Dia. cm.	Area sq. cm.	Length cm.
No. 5.	.421	.14	1.3
No. 2.	.575	.26	3.1
No. 00.	.794	.495	3.1
Paper.	1.15	1.04	3.1

The hemispherical end of the capsule cylinder was removed, and a paper disc inserted in its stead, thus giving a flat end to the cylinder. The caps were removed and two or more joined end to end to form a cylinder of desired length.

EXPERIMENTS WITH ROTATING MILL.

A small mill was constructed by fastening four No. 00 capsule cylinders each 1.7 cm. long, on cardboard arms as shown in Fig. 2. The arms of the mill were each two centimeters long. The mill was mounted, by means of a glass pivot, upon a fine steel point which was fastened to the end of a long rod. By means of this

rod the mill could be carried to any desired part of the stationary wave. The shorter pipe which was used in this experiment was placed in a vertical position. The rod bearing the mill was introduced through the stop at the lower end. The mill was thus enclosed in the pipe with its plane of rotation perpendicular to the stream-lines, *i. e.*, the vibrations were always perpendicular to the axes of the cylinders.

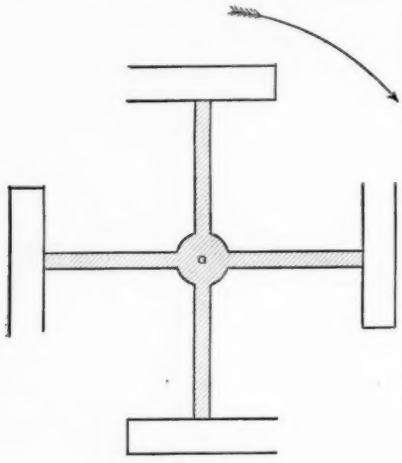

Fig. 2.

Matters being thus arranged when the pipe was blown, the mill rotated with a high velocity. The rate of rotation was greatest at the middle of the loop and it came to rest at the nodes.

A series of experiments were made to determine the variation of the rate of rotation with the position along the wave. A constant pressure of blowing was maintained throughout the experiments. The zero of the scale on the pipe is at the node at the diaphragm. A stroboscopic disc was used to count the rotations. The results of a number of experiments are given in the table below:

TABLE II.

Position along Pipe.	Relations per Second.	Position along Pipe.	Relations per Second.
0	0	27	9.00
4	.92	30	8.74
9	4.69	34	7.70
14	7.00	39	6.43
19	8.12	44	3.70
22	8.44	49	.77
25	8.80	52	.0

This table is plotted in the curve shown in Fig. 3. The ordinates are rates of rotation per second and the abscissæ are distances along pipe. The full line is the observed curve and the broken

line is a sine curve. The agreement of the observed curve and the sine curve is very close.

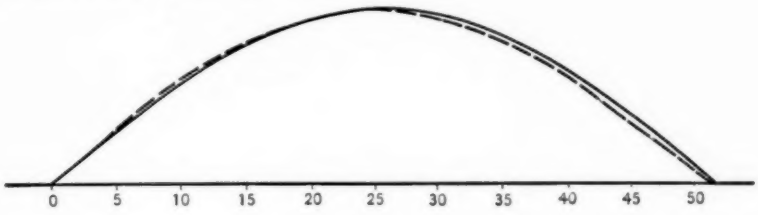

Fig. 3.

The force driving the cylinder across the pipe was measured by means of a torsion balance mounted in the longer pipe as shown in Fig. 1. Two cylinders L are mounted at the end of a cardboard arm, their plane being perpendicular to the pipe. They are placed a small distance apart to allow the vibration of the air between them. When the pipe was blown the cylinder moved towards the wall of the pipe and the torsion head was turned until the cylinders came back to their zero position. The amount of torsion was indicated by the pointer p on the scale s.

The Effect of Area of Cross-section of the Cylinders.

In making this investigation the mounted cyliders of various sizes were brought to the middle of the loop, the force being a maximum at that point. A table is given below of the degrees of torsion for the various cylinders. The sizes corresponding to the number of cylinders are given in Table I. The readings have all been reduced to the same area (1 sq. cm.) and the same length of arm. The manometer pressures are in centimeters of mercury.

It will be observed that for low pressure the small cylinders are affected the most. The No. 00 cylinders experience the largest force for moderate pressures as those near the pressure of maximum efficiency, while for the highest pressures the paper cylinder is most strongly affected. The No. 5 and No. 2 cylinders give almost identical results.

The shape of the body in the sound-wave also affects its behavior in a marked manner. Instead of the cylinders a hollow rectangular parallelopiped was used, which was 30 mm. long, 20

TABLE III.

Degrees of Torsion.

Pressures.	No. 5.	No. 2.	No. 00.	Paper.
1½	20	22	10	8.6
2	66	64	89	46
3	198	215	320	176
4	362	306	410	354
5	460	409	550	620
6	530	500	690	630
7	644	610	750	745
8	715	714	830	820
9	811	780	920	969
10	862	834	1000	1090
11	898	891	1030	1220
12	925	907	1055	1318
13½	928	923	1080	1360
15	927	923	1060	1260
16	Overtone.			

mm. wide and 2 mm. thick. The area of the closed end was 40 sq. cm. This was placed in the sound-wave successively in two positions. (1) The 20 mm. edge was placed *perpendicular* to the directions of the stream-lines (position A). (2) The 20 mm. edge was placed *parallel* to the direction of the stream-lines (position B).

The results of the experiment are given in Table IV. *A* and *B* are the readings obtained at the given pressures in the two positions mentioned above. *A'* and *B'* are the same readings reduced to the

TABLE IV.

Degrees of torsion.

Pressures.	*A*	*B*	*A'*	*B'*	*C*
1	2.5	0	3.8	0	5
2	45	0	68	0	89
3	116	5	174	7.6	320
4	150	30	228	46	410
5	179	92	270	140	550
7	190	120	288	185	750
10	193	150	290	228	1000
12	198	160	300	245	1055
15	228	215	345	325	1060
17	255	256	436	436	

area of 1 sq. cm. and same length of arm used with No. 00 cylinders in Table III. Column *C* contains the results for No. 00 cylinders brought over from Table III. for comparsion.

The force depends quite decidedly on the position of the parallelopiped with reference to the stream-lines except in the case of large amplitudes, when the values approach and become equal just as the pipe passed over into the second overtone. By comparison with *C* it will be noticed that the rectangular shape gives much less effect than the cylindrical.

Variation of the Force Along the Stationary Wave.

The No. 2 capsule cylinders were used in these experiments. Two of them were fastened to the end of the arm of the torsion balance. The arm was 5.33 cm. long. The torsion balance was moved along the pipe and readings taken at intervals from near the diaphragm to the stopped end. The pipe was blown at the constant pressure of 3 cm. of mercury throughout. The note obtained at this pressure was quite free from overtones. The results of the experiments are given in Table V.

Table V.

Position along Pipe.	Torsions.	Sq. root of Torsion.	Position along Pipe.	Torsions.	Sq. root of Torsion.
0	0°	0	29	190°	13.8
6	36	6	32	173	13.1
11	79	8.9	35	145	12
16	148	12.1	39	102	10.1
21	185	13.6	42	73	8.6
25	194	13.9	48	25	5.
27	198	14.1	54	0	0

This table is plotted in Fig. 4. The abscissæ are positions along pipe and the ordinates are *square roots* of torsions. The full line is

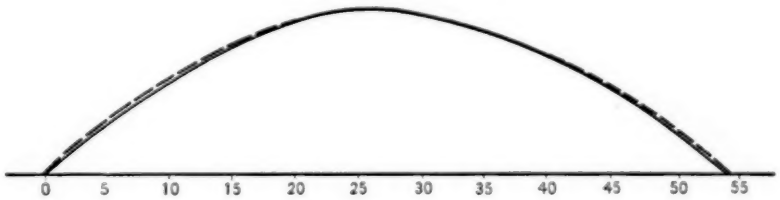

Fig. 4.

the observed curve and the broken line is a sine curve. The agreement of the two curves is quite close and indicates that the cylinders experience a force that is proportional to the square of the amplitude of vibration at any position.

EXPERIMENTS PERFORMED IN VARIOUS GASES.

The portion of the organ-pipe between the diaphragm and the stopped end forms a closed chamber which is kept free from all disturbances except the vibratory motion of air or gas. Various gases were introduced into this chamber and the force determined as before. The stationary wave that was formed was transmitted through two media: the gas back of the diaphragm and the air in front of it. Both pipes were used in these experiments, those with the shorter pipe are described first.

The stop was fixed and the length of the pipe could not be altered. When a dense gas as carbon dioxide was used, the pitch was lowered and the node was moved a little toward the stopped end. The pitch was raised when illuminating gas and hydrogen were used, and the node, at least in the case of the illuminating gas, was moved toward the mouth. The rise in pitch was quite noticeable with hydrogen. Measurements were made in the middle of the loop as before, care being taken to keep the pressure of blowing constant throughout the series of experiments.

The mean results of a number of experiments are given in the table below, the torsion readings in air as well as its density being taken as unity.

	Torsion Deflections.	Density of Gas.
Air	1.	1.
CO_2	1.47	1.52
Illum. gas	.77	.75
Hydrogen	.064	.069

The force obtained is closely proportioned to the density of gas used. The above results were obtained when the pipe was blown at moderate pressures. The relation does not hold for all pressures, as will be shown later in this paper.

The stop of the shorter pipe was fixed, and the node, when the chamber contained air, was at the diaphragm. The densities of car-

bon dioxide and illuminating gas do not differ from air sufficiently to displace the node very much and the change of pitch obtained was approximately as should be expected. When hydrogen was used the pitch of the pipe was raised, but not at all in proportion to the inverse of the square root of its density. The pitch was such as to throw the node, had a simple wave been formed, just outside the mouth of the pipe. This would seem to indicate that a simple wave was not formed in this case, but that the mode of vibration was influenced in an indeterminate manner by the air space between the diaphragm and the mouth. The compartment of air between the diaphragm and the mouth possibly acted partially as a pipe having a stop at the position of the diaphragm. On account of the small density of the hydrogen its energy was inconsiderable compared to that of the air column, so that the tone obtained was a compromise between that natural to the air space outside the diaphragm and that natural to the hydrogen column within.

The pitch natural to the pipe with a stop at the position of the diaphragm is about 330 vibrations per second, while that natural to the hydrogen column behind the diaphragm would have been above 1,200 vibrations per second. This would seem to affirm that the characteristic pitch was largely determined by the air column in front of and not by the hydrogen column back of the diaphragm.

The longer pipe was constructed at the suggestion of Dr. F. L. Tufts for the purpose of overcoming these difficulties. This pipe had a movable stop, which was placed so as to give the same note as the shorter pipe, and then the diaphragm was adjusted to the node. The shorter pipe was used as a standard of pitch. On introducing carbon dioxide the stop was moved up until the pipe spoke in unison with the shorter one. In the case of illuminating gas or hydrogen the stop was moved back until unison was obtained. The positions of the stop were: for CO_2, at 45 cm.; for air, at 54 cm.; for illuminating gas, at 62 cm., and for hydrogen, at 188 cm. from the diaphragm. These distances are nearly equal to one-half of the length of the stationary wave formed in each case. This arrangement made the conditions at the mouth and diaphragm constant for all the gases. The form of the exterior wave was not altered.

The efficiency curves of the organ-pipe for the gases were obtained by this arrangement, the torsion balance being moved so as to be in the middle of the loop of the stationary wave in all cases. The pipe was first blown at low pressure, and then the pressure was increased until it passed over into the next overtone. Table VI. contains the results of the experiments with various gases. The range of pressure of blowing in the case of hydrogen was so small that it was necessary to use a water manometer and afterward reduce the pressure to the corresponding mercury manometer readings. The torsion balance carried two No. 00 cylinders each 3.1 cm. long.

TABLE VI.

	Degrees of Torsion.			*Hydrogen.*	
Pressure.	**Air.**	**Illum. gas.**	**CO_2.**	**Pres.**	**Torsion.**
1	9	5	12	1.22	1.3
1½	69	45	90	1.47	3.8
2	195	120	290	1.62	10.9
2½	400	275	530	1.76	15.
3	510	365	690	1.91	26.
4	760	530	880	2.06	34.
5	920	670	1100	2.20	53.
6	1120	875	1170	2.41	64.
7	1230	1140	1200	2.50	overtone.
8	1250	1160	1220		
9	1260	1240	1210		
10	1270	1260	1230		
11	1290	1260	1230		
12	1320	1210	1250		
13	1470	1130	1280		
14	1500	overtone.	1260		
15	1570		1250		
16	overtone.		1350		
17			1520		
18			1560		
19			1560		
21			1500		
22			overtone.		

This table is plotted in Fig. 5, with pressures of blowing as ordinates and the square roots of torsion as abscissæ. It will be shown later that the amplitude of vibration is proportional to the square root of the force acting on the cylinders, hence the curves

obtained represent the relation between the pressures of blowing and the amplitude of vibration of the gas particles in the middle of the loop.

As a result of so me experiment conducted by Dr. F. L. Tufts, it has been found that the cube of the velocity of efflux of air from the slit of an organ-pipe is approximately proportional to the square of the pressure. The energy of an escaping jet of air is also proportional to the cube of the velocity, hence the energy delivered to the pipe is proportional to the square of the pressure of blowing. The energy contained in the vibrating air is proportional to the square of the amplitude, consequently the torsions represent the energy converted into sound.

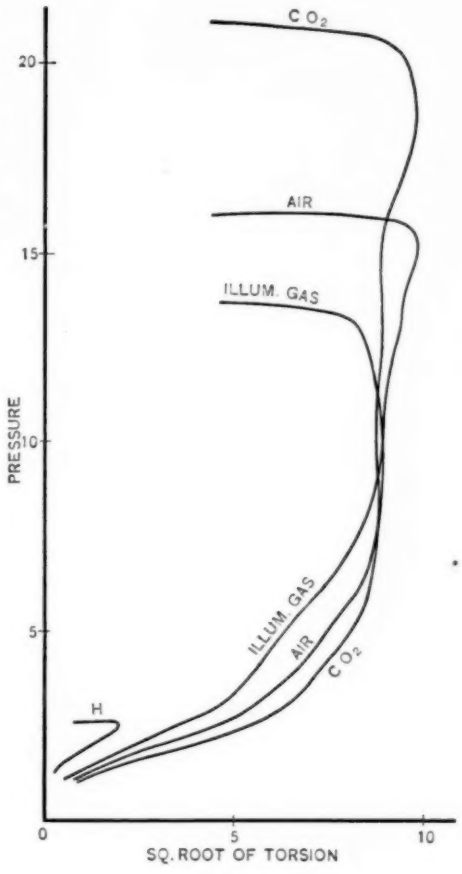

Fig. 5.

The curves of relation between torsions and squares of pressures plotted in Fig. 6, are the efficiency curves of the organ-pipe. The pressure of maximum efficiency is indicated by the ordinates of the points of tangency of the tangents to the curves through the origin. This pressure was found to be nearly the same for all gases, being somewhat less for hydrogen. In the case of carbon dioxide, air and illuminating gas it was about 2.3 cm. of murcury. The torsions obtained at this pressure are given in the table below, the values for air as well as its density being taken as unity.

This is nearly the same result obtained with the shorter pipe.

TABLE VII.

	Torsions.	Density of Gas.
Air	1.	1.
CO_2	1.53	1.52
Illum. gas	.71	.75
Hydrogen	.153	.069

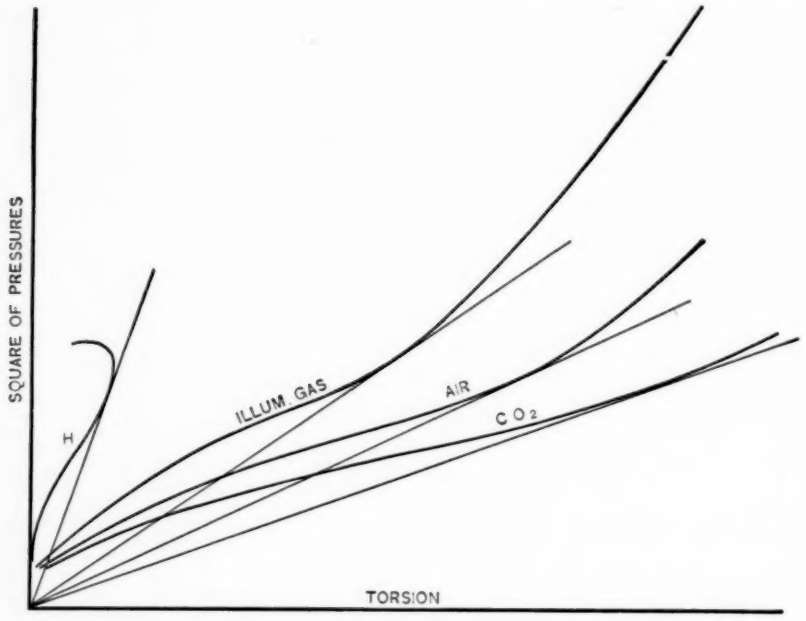

Fig. 6.

In the experiments the results of which are given in Table VI., the pressure was increased from zero until the note passed over into the next overtone. The pressure at which the second overtone was obtained was not sharply defined. At a high pressure the tone was in an unstable condition, so that when the finger was brought near the mouth of the pipe, the equilibrium was destroyed and the second overtone obtained. The pressure at which the second overtone appeared varied with the gas. The length of the pipe varied inversely as the density of the gas, so this shows the well-known fact that the longer a vibrating column, the more easily it breaks into shorter waves. The hydrogen wave being very long bu a small pressure was necessary to force the next overtone.

The rates of rotation of the mill previously mentioned were also taken in the various gases. The shorter pipe was again used for this purpose. It was placed vertically and the mill introduced from below as before. The pressure of blowing was kept constant throughout the experiments. The mean results obtained are given below, the rate of rotation in air as well as its density being taken as unity.

Air.	Illum. Gas.	CO_2.	Hydrogen.
1	1	1.04	.59

The rate is apparently constant for all gases, although the force acting on the mill to produce this rotation is proportional to the density of the gas. This can be explained by the circumstance that the resistance to motion is also proportional to the density. The deviation from this result in the case of hydrogen is probably due to the fact that the friction of the supporting pivot was not an inconsiderable quantity compared to the total resistance experienced by the cylinders, and this factor is proportionately larger in the case of hydrogen.

Discussion.

This phenomenon is another instance of the relation between pressure, density and velocity of a fluid first expressed analytically by Daniel Bernouilli.[1] A fluid in motion is less dense than the same fluid at rest. The air within the small cylinder remains nearly at rest, while that without is in rapid motion. The air on the outside is less dense than that within the cylinder. The force exerted is due to the difference in density and pressure on the two sides of the closed end of the cylinder. It is evident from the formula deduced below, that if the force is measured in absolute units then a value for the velocity and amplitude may be found.

The relation between the velocity, pressure, and density of a fluid may be expressed by Bernouilli's equation since for this case the average state of the fluid only is under consideration.

$$\int \frac{dp}{\rho} = R - \tfrac{1}{2}u^2.$$

[1] Hydrodynamica, Argentorati, 1728.

R is the potential due to external forces and is negligible in this case; hence

$$\int \frac{dp}{\rho} = -\tfrac{1}{2}u^2.$$

The adiabatic gas relation gives $p = C\rho^\gamma$, where C is a constant and γ is the ratio of the specific heat at constant pressure to that at constant volume.

$$C^{\frac{1}{\gamma}} \int p^{-\frac{1}{\gamma}}\, dp = \tfrac{1}{2}u^2.$$

$$\left[\frac{\gamma}{\gamma - 1} C^{\frac{1}{\gamma}} p^{\frac{\gamma-1}{\gamma}}\right]_1^2 = \left[-\tfrac{1}{2}u^2\right]_1^2.$$

$$\text{Let } \frac{\gamma - 1}{\gamma} = n \quad \text{and } A = \frac{\gamma}{\gamma - 1} C^{\frac{1}{\gamma}}$$

$$A(p_2^n - p_1^n) = -\tfrac{1}{2}(u_2^2 - u_1^2)$$

$$\frac{1}{n} \cdot \frac{p_2}{\rho}\left[1 - \left(1 - \frac{p_2 - p_1}{p_2}\right)^n\right] = -\tfrac{1}{2}(u_2^2 - u_1^2)$$

Expanding and neglecting all powers above the first, since $\frac{p_2 - p_1}{p_2}$ is a very small quantity, the equation reduces to, $u_1^2 - u_2^2 = 2\frac{p_2 - p_1}{\rho}$.

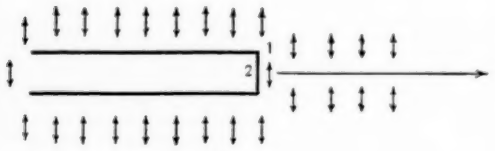

Fig. 7.

The cylinder is in the moving air as shown in Fig. 7. u_1 represents the velocity of the air outside the cylinder, and u_2 represents the velocity within the cylinder next to the closed end, while p_2 and p_1 are the pressures on the two sides of the closed end. If the air within the cylinder is at rest u_2 is zero, hence

$$u_1^2 = 2\frac{p_2 - p_1}{\rho} \qquad (1)$$

The constant of the torsion wire as previously given was .3° per dyne of force. The wire was 16 cm. long and the arm was 4.82 cm.

in length. The maximum deflection obtained was 1570°, hence the force was 68.26 dynes per square centimeter.

The force experienced by the cylinders is the mean of all the instantaneous values due to the velocity of the air at any instant. The force is proportional to the square of the velocity, hence the mean force will not directly give the mean velocity in equation (1).

The force F at any instant is equal to $\frac{1}{2}\rho u^2$, where u is the instantaneous velocity. Let A be the maximum displacement, and x any displacement at time t.

$$x = A \cos nt.$$

$$n = \frac{2\Pi}{T},$$

where T is the periodic time.

$$\frac{dx}{dt} = u = -An \sin nt.$$

Also

$$\frac{\int F dt}{\int dt} = p_2 - p_1,$$

the mean force experienced by the cylinders.

Therefore:

$$\frac{\int F dt}{\int dt} = \frac{\frac{1}{2}\rho \int n^2 A^2 \sin^2 nt \, dt}{\int dt}.$$

The limits of integration are 0 and $\frac{1}{2} T$; hence,

$$p_2 - p_1 = \rho A^2 \frac{\Pi^2}{T}$$

and

$$A = \frac{T}{\Pi} \sqrt{\frac{p_2 - p_1}{\rho}}.$$

The frequency of the pipe when blown at high pressure was 338 per second.

Therefore:

$$A = .216 \text{ cm.}$$

The total excursion of the particles was $2A = .432$ cm.

This must be a minimum value, that is less than the real value as the investigation above assumes that the air within the cylinder is at rest, and that there is no friction between the surface of the cylinder and the vibrating air. The effect of such friction would be to decrease the velocity and surround the cylinder with a skin of air of little greater density.

Among the methods that have been devised to determine the amplitude of vibration in a stationary wave, that of Raps[1] might be mentioned. He measured the change in density at the node of an organ-pipe by a rather complex mechanical method and deduced the amplitude from such measurements. He obtained an amplitude of .34 cm., the pipe speaking its fundamental of 184 vibrations per second. The force that might have been obtained had small cylinders been used would have been 50.25 dynes per sq. cm. This does not differ greatly from the maximum force obtained in the experiments above described, although from the very nature of the investigation accurate comparison of results is not possible.

A consideration of the curves of efficiency in Fig. 6 shows that the pressure of maximum efficiency for carbon dioxide, illuminating gas and air is nearly the same, also by Table VII. the force at this pressure is proportional to the density of the gas. This confirms experimentally the statement of Lord Kelvin[2] in his letters to Guthrie, that the change in density, the conditions being the same, would be proportional to the density.

At the blowing pressure of maximum efficiency the value of u in equation (1) is constant and as the frequency is the same, the amplitude of vibration is the same for all gases.

The energy of the sound produced would be proportional to $\frac{1}{2}\rho u^2$, and since the velocity u was constant, the energy of the sound should be proportional to the density of the gas. This was observed to be the case. The volume of sound emitted by the pipe was greater with the carbon dioxide, than with the air wave, while in the case of hydrogen it was very weak.

The curves in Fig. 5 show that at pressures from 9 cm. to 11 cm. of mercury the force was the same for the three gases, hence at

[1] Wied. Ann., New Series, XXXVI., p. 273.
[2] Phil. Mag., XLI., p. 405.

these pressures the amplitudes were inversely as the square roots of the densities. The less the density the greater the velocity, so that the energy of the sound produced was the same for the three gases at these pressures.

There are a number of natural phenomena that have their explanation in this relation between pressure, density and velocity of a fluid. Perhaps the best known one is the Clemént effect, in which a flat disc is held against an escaping jet of air. This is also illustrated by the ball-nozzle so extensively in use. The investigations of Hallock[1] on the Clemént disc show that the pressure is much decreased at the point where the velocity is greatest.

Another phenomenon is the acoustic attractions of Guthrie which Lord Kelvin[2] has shown to depend on this law also.

A very striking effect is the rotating resonators of Dvořák,[3] the action of which has been explained by Lord Rayleigh.[4] Still another effect is the setting of a disc across the stream-lines in a sound-wave obtained by Lord Rayleigh,[5] and which has been used by Boys[6] for the detection of faint sounds.

The magnitude of the force described in this paper is greater than the tendency of a disc to set across the stream-lines. An instrument designed on the plan of Boys' using small cylinders instead of a disc would probably be quite as sensitive as the one constructed by him.

PHYSICAL LABORATORY, COLUMBIA UNIVERSITY,
May 1, 1901.

[1] Science, Aug. 2, 1895.
[2] Phil. Mag., XLI., p. 405.
[3] Pogg. Ann., CLVII., p. 42; Wied. Ann., III., p. 308.
[4] Theory of Sound, Vol. II., p. 42.
[5] Phil. Mag., 5th Series, Vol. XIV., p. 186.
[6] Nature, Vol. XLII., p. 604.

ON THE HEAT EVOLVED WHEN LIQUIDS ARE BROUGHT IN CONTACT WITH POWDERS.

BY C. E. LINEBARGER.

INTRODUCTION.

THE fact that there is a rise of temperature when liquids are mixed with fine powders was first noted by Pouillet,[1] and his results have been confirmed and extended by a number of subsequent investigators.[2] Nearly all of these investigations were purely thermometric, and the few that were calorimetric either employed rather crude methods or but few liquids, as water, alcohol and benzene. The object of this paper is to present the results of a number of determinations of the heat effect due to the bringing of different simple liquids in contact with silica powders of different degrees of fineness in order to ascertain the influence of the nature of the liquid as well as the fineness of the powder on the heat effect. The starting point of the investigation was an attempt to experimentally verify certain theoretical relationships between heat and surface energy, sketched by Gibbs;[3] as the experiments did not, however, corroborate the relationships, only the experimental work will be given here.

MATERIAL.

The powders were all of precipitated silica, several specimens of which from different sources were used. The method of preparation renders the assumption that they consist of approximately

[1] Ann de chim. et de physique, XXII., 141 (1822).

[2] Junck, Pogg. Ann., CXXV., 292 (1865). Cantoni, Rendiconti del R. Istituto Lombardo, VIII., 135 (1866). Melsens, Mémoires del l'Academie de Belgique, XXIII. (1873). Chappuis, Wied. Ann., XIX., 21 (1883). Wiedemann and Lüdeking, Wied. Ann., XXV., 145 (1885). Meissner, Wied. Ann., XIX., 114 (1886). Gore, Phil. Mag., XXXVII., 306 (1894). Martini, Atti del R. Istituto Veneto, VIII. (1896); IX., (1897), XII. (1900).

[3] Thermodynamische Studien, page 316.

spherical granules of uniform size quite plausible. As a matter of fact, if a microscopic slide be dusted over with precipitated silica, and the powder examined under a high power, the particles are seen to be of fairly uniform size. By means of a stage micrometer the diameters of a large number of these granules were measured, from the average of which the surface and volume of an average granule could be calculated. Such an examination of four samples from different sources, one of which was furnished by Professor Martini[1] and was the same as that used by him in his investigations, resulted in an average diameter of 0.0005 cm. All four samples gave practically the same results. Two stage micrometers were employed, and measurements of several hundred different granules of each sample made. The silica having granules of this size will hereafter be designated as silica I.

A fifth sample (a pound bottle of Koenig's) was found to consist of granules of an average diameter of 0.00096 cm. This sample will be called silica II. It is noteworthy that the granules of silica II. happened to have about twice the diameter of those of silica I.

The specific heat of precipitated silica does not seem to have been determined. From the determinations of the specific heat of various forms of quartz by Regnault,[2] Joly,[3] Bartoli,[4] and Pionchon,[5] the specific heat of precipitated silica is very near to 0.2, and that value has been used in this work. The specific heat of the glass container has also been taken as 0.2.

The methods of preparation of the liquids as well as some of their physical constants are given in what follows:

Benzene.—Eight pounds of "c. p." benzene were treated many times with small portions of strong sulphuric acid to remove traces of thiophene, and fractionally crystallized until about five pounds were obtained melting at 5°.38 to 5°.44 (corr.). It was then distilled, the first and last runnings being rejected. It boiled at 80°.1 (corr.) under a pressure of 757.1 mm. of mercury.

[1] Loc. cit.

[2] Ann. de chim. et de physique (3), I., 129 (1841).

[3] Proc. Roy. Soc., XLI., 250 (1887).

[4] Nuovo Cimento (3), XV., 5 (1884).

[5] Comptes rendus, CVI., 1344 (1888).

Its specific heat was taken as 0.42 from Pickering,[1] DeHeen and Deruyt's,[2] Schiff's[3] and Regnault's[4] determinations.

Toluene.—Five pounds of toluene were fractionally distilled until about three pounds were obtained boiling at 109°.9 to 110°.0 (corr.) under a pressure of 757.5 mm. This portion was redistilled with a short column and the first and last runnings rejected.

Its specific heat was taken as 0.42 from the results of DeHeen and Deruyt,[10] and Schiff.[5]

Nitrobenzene.—Five pounds were fractionally crystallized until about three pounds resulted showing an almost constant melting point. This was distilled, the first and last runnings being rejected. From Regnault's[6] measurements its specific heat may be taken as 0.337.

Pyridine.—Five pounds of "c. p." pyridine after thorough drying were fractionally distilled with a long column. After three distillations about two pounds were obtained boiling at 114°.6 to 114°.8. Luginin[7] gives its specific heat as 0.4315.

PREPARATION OF THE POWDER.

Precipitated silica absorbs large amounts of air and other gases as well as the vapors of liquids. These can be removed only by heating to a high temperature in a vacuum. As the presence of absorbed substance has a considerable influence on the heat effect of wetting the silica with liquids, it has to be carefully removed to insure uniform results. This was done as follows: Large test-tubes about 2.5 cm. in diameter were drawn down to a narrow neck at about 6 cm. from their closed end, heated in an air-bath for some time to dry them thoroughly, cooled and weighed to tenths of a milligram. The silica was heated for an hour or so in an iron crucible at a red heat. While still hot, the proper amount was introduced into one of the tubes which was grasped with a test-tube

[1] Proc. Roy. Soc., XLIX., 11 (1890).
[2] Bull. de l'Academie de Bruxelles (3), XV., 168 (1888).
[3] Liebig's Ann., 234, 300 (1886).
[4] Mémoires de l'Academie, XXVI., 262 (1862).
[5] Liebig's Ann., 234, 300 (1886).
[6] Ann. de chim. et de physique (3), IX., 322 (1843).
[7] Comptes rendus, CXXVIII., 366 (1899).

holder and heated to incipient redness until no more gas or vapor was given off. It was then without delay connected with a Boltwood air pump, and the evacuation started. When the pressure had fallen to less than a millimeter, the tube was heated as hot as was possible without the distortion of the glass, and then sealed off with a blowpipe flame. Usually some gas was driven off by this last heating, but not in sufficient amount to affect the gauge. The bulb thus filled with silica and the remnant of the test-tube were then weighed separately in order to ascertain the weight of the silica as well as that of the container.

Apparatus.

The *calorimeter* was a cylindrical vessel of thin, nickel-plated brass, 6 cm. high and 7 cm. wide, holding about 250 cc. This was held firmly inside a glass beaker by means of conical cork supports glued to the glass. In the same fashion this beaker was placed inside a larger beaker, which in turn stood on cork supports inside a battery jar. There were thus three layers of glass and of air separating the calorimeter laterally from the outside air. The battery jar was tightly closed with a thick piece of paraffined wood pierced with holes for the passage of the thermometer and the device for breaking the bulb. The whole was placed in a fume chamber where the temperature could be kept almost constant for several hours. The water-equivalent of the calorimeter was found by special experiment to be 3.99 cal.

The *thermometer* was a Beckmann instrument graduated in hundredths, and made by F. O. R. Götze in Leipzig. The readings were taken with a good hand lens so arranged as to reduce the error due to parallax to a minimum. The water-equivalent of the thermometer was found by special experiment to be 0.94 cal.

The "*crusher.*" To break the bulb when immersed in the liquid in the calorimeter, after ineffectual efforts to employ to advantage a hammer with sharp points also immersed in the liquid, the following "crusher" was devised. A piece of thin brass tubing, 3.2 cm. in diameter and 2.8 cm. long was cut out and filed down so that it took the form of two rings connected by two narrow cross-bars. A small nut was soldered in the middle on the outside of one of

these cross-bars and around it a tube of thin brass, 0.4 cm. in bore and 4 cm. long. A piece of glass tubing was fastened with cement over one end of this tube, thus serving as a handle of poor-conducting material. In the nut played a screw 6 cm. long, the upper end of which was flattened so as to engage in a split in the end of a brass rod a little longer and a little narrower than the glass tube. When a bulb containing the silica was placed in the cut-out brass tubing, the screw could be turned down so as to hold it securely. A turn or so more of the screw then sufficed to break the tube. This ordinarily broke in a few pieces so that the powder was almost instantaneously introduced into the liquid. The shape of the "crusher" was such as to make quite an efficient stirrer. The water-equivalent of the "crusher" was 1.35 cal.

Mode of Making a Determination.

The calorimeter is filled about three-fourths full of the liquid (which had been kept standing in the fume chamber so as to be at the same temperature as the apparatus) and weighed to centigrams. It is unnecessary to weigh the liquid with a greater accuracy than this as the evaporation during the determination amounts to several centigrams. The calorimeter is then placed within the beaker, and the tube filled with the powder clamped in the "crusher" and immersed in the liquid which rises nearly to the glass handle. The cover to the jar is set on and the thermometer inserted.

Readings of the thermometer are taken at intervals of about ten minutes (care being taken that the temperature of the fume chamber be as constant as possible and that the liquid be stirred occasionally) until they do not differ by more than 0°.05. When this is the case the thermometer is read every minute, the liquid being stirred for about fifteen seconds after each reading and the thermometer being smartly tapped with a pencil. If the readings change uniformly by less than 0°.005, for at least ten minutes, the bulb is crushed, the brass rod removed, and gentle but thorough stirring kept up until the readings are again uniform. Commonly this is the case in less than two minutes. The thermometer is again read at intervals of one minute with stirring of fifteen seconds' duration as before for ten minutes. The change of temperature can then be calculated in the customary way, and is known to within 0°.005.

Calculations and Data.

It was assumed in the calculations that only the calorimeter, thermometer, "crusher," container, powder and liquid were to be taken into consideration. The water-equivalents of these were added together and multiplied by the temperature change. To refer all heat effects to that due to one gram of precipitated silica, this product was divided by the weight of the powder taken in each particular experiment. The data are given in the following table; the superscriptions render any detailed explanation unnecessary.

Silica.	Liquid.	Weight of Silica.	Weight of bulb.	Weight of liquid.	Rise of Temperature.	Cal. per gram of Silica.
I	H_2O	4.8467	4.8060	130.04	0.479	13.80
I	H_2O	4.3528	4.4411	129.98	0.435	13.81
II	H_2O	4.4308	4.5295	155.70	0.188	6.90
I	$C_6H_5NO_2$	4.1826	6.6047	174.49	0.744	11.21
I	$C_6H_5NO_2$	4.8915	6.1085	167.00	0.822	10.88
II	$C_6H_5NO_2$	4.5865	6.8934	179.51	0.443	6.67
II	$C_6H_5NO_2$	4.4446	4.2122	159.92	0.444	6.02
II	$C_6H_5NO_2$	5.1788	6.3000	170.99	0.482	6.13
I	C_7H_8	5.1135	6.8186	125.70	0.802	9.61
I	C_7H_8	5.4251	4.2354	107.41	0.750	7.55
II	C_7H_8	4.2034	6.0508	105.09	0.388	4.84
I	C_6H_6	6.4765	6.0427	126.30	0.428	4.09
II	C_6H_6	4.9773	5.8233	180.00	0.336	4.06
II	C_6H_6	5.9091	7.0179	130.08	0.383	4.11
I	C_6H_5N	5.1881	6.2174	142.71	0.876	11.84
I	C_6H_5N	4.5984	7.8442	146.40	0.797	12.46
II	C_6H_5N	5.3244	6.7236	140.00	0.382	4.89
II	C_6H_5N	5.4922	6.9446	140.00	0.409	5.07

Discussion of Results.

The relative amount of liquid does not seem to influence the heat effect. A certain minimum quantity is necessary to produce the maximum heat change, but any excess of that amount has no perceptible influence. The heat effect per unit mass of the powder is the same for the same liquid at the same temperature, provided this minimum amount be present.

The finer the powder, the greater the heat effect, seems in general to be true. In the case of water, toluene, pyridine and nitrobenzene, the heat effect with silica I. is about twice that of silica II.,

and the granules of the first powder are about double the size of those of the second. But in the case of benzene no such differences are apparent. Here about the same heat effect is produced with either powder. While qualitatively it undoubtedly holds that the finer the powder, the greater the heat effect, it has not been shown quantitatively that such is the case. It is noteworthy that the different liquids do not vary much in their heat effects; water gives the largest and benzene the smallest. But pyridine and nitrobenzene, although very similar to benzene chemically, exhibit heat effects which approach that of water.

In conclusion, it is a pleasant duty to thank the members of the Board of Education of Chicago for their kindness in granting the writer the necessary means for carrying out this work. It is perhaps unique in the history of secondary schools that a board has voluntarily set aside a fund to aid in the prosecution of research in natural science.

Chicago, May 3, 1901.

ON THE DENSITY OF ICE.

By H. T. Barnes.

IN a very complete and comprehensive paper published in this Review by Professor E. L. Nichols,[1] some interesting new points were brought out in connection with the density of ice of different ages, besides an exhaustive résumé and criticism of our knowledge of the absolute value of the density of ice.

It appears that this is subject to variation, depending on the manner of formation, and according to Nichols' measurements a difference of two parts in one thousand is noted between old and new ice. The rapidity of formation apparently fixes, at least temporarily, the value of the density, but as is shown, the greater density, possessed by new natural ice or artificial ice which is formed rapidly at a low temperature, does not persist, but tends to pass to a lower value which is probably more nearly equal to the true density.

The many and varied phenomena connected with the formation of river ice in our northern climate at Montreal makes a study, such as this one of much interest.[2] Until the work of Nichols appeared, there were no decisive experiments involving the actual measurement of a variation in the density of ice, but since such has been unquestionably indicated, the possibility of the varying density of the ice crystals, which are formed exceedingly rapidly throughout the mass of a quickly-flowing river by the admixture of cold air, suggests itself. To account for certain phenomena, this seems to be a necessary premise, but until more decisive measurements have been attained little definite use can be made of it.

In regard to the influence of age on the density of ice, a matter of some interest, the author undertook during the past winter a few experiments, with the kind aid of Mr. H. Lester Cooke, B.A.,

[1] Physical Review, 8, 21 (1899).

[2] See the author's papers on river ice formation, Trans. Roy. Soc. Can., 2, 37 (1896) 3, 17 (1897), 5, 17 (1899).

to determine the difference, if any, between ice two years old and ice which had been recently formed during the winter. Blocks of beautifully clear ice, which had been cut during the winter of 1898–99 and during the winter of 1899–1900 from the St. Lawrence River, were kindly supplied to us by Mr. Beckets from the storage houses of the City Ice Co., together with several similar blocks taken from the river. These were kept intact, carefully labeled and buried in a pile of soft, newly fallen snow. The chief difficulty appeared to be to select a suitable method for the determination of the density, which would be easy of operation and sufficiently accurate to show the small differences to be expected. It was finally decided to weigh a small block of ice directly in water at 0° C., in preference to selecting any of the other methods hitherto used. At first sight this method appears to be open to every objection, but, by suitable arrangements of the experimental conditions, it has undoubtedly yielded us the most satisfactory results in the shortest time. It is, of course, essential to have both the ice and water absolutely at the zero point, which, with the great supply of ice and snow available during the winter for the production of freezing-point mixtures, offers no difficulties whatever. The method consists in surrounding a copper vessel (Fig. 1), by a mixture of pure snow and water, and thereby cooling the air in the vessel to zero. Through a narrow neck in the cover of the vessel, which is securely bolted down air-tight, passes a light suspension from a weighted grip, consisting of three fingers for clutching the ice, to one of the arms of a sensitive Oertling balance. Near the bottom of the vessel a side tube is fastened connected by rubber with a copper or glass tube passing up through the mixture. By pulling out the copper tube, the surrounding water at zero runs in and fills the vessel completely into the narrow neck. Small particles of ice carried in through the side

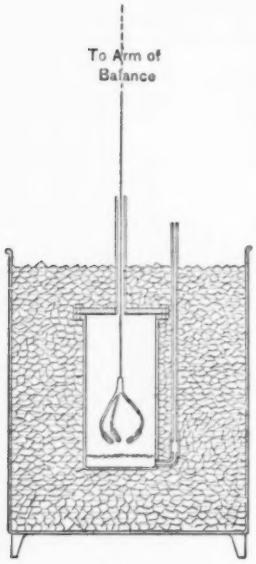

Fig. 1.

tube are filtered out by a fine wire gauze placed near the bottom of the vessel. The purity of the snow and water was a matter which demanded special attention, as well as thecleanliness of the copper vessels employed.

Careful determinations of the specific gravity of the suspension were made, under exactly similar conditions to those existing during an experiment, the water rising to the same point in the neck and including the same, or approximately the same, length of suspension wire in each case.

To carry out an experiment, blocks of ice were broken off from the main lump, in such a way as to include clear pieces free from cracks or air bubbles, and were then rounded off on the sharp edges by scraping and washing in cold water. Pieces of about 200 grams were thus prepared from the different lumps, and set aside under a protective cover surrounded by snow. The copper vessel having been carefully dried and partially packed in snow, the cover was removed and the whole taken outside the building into the air, which was not far from the freezing point during the days on which the measurements were made. The piece of ice selected was then carefully wiped dry with filter paper and a linen rag, and, without coming in direct contact with the hand, was introduced into the three-prong grip and quickly inserted in the copper vessel. The cover was then securely fastened down, and the complete vessel immersed in the snow and water. The mixture was then taken to the laboratory, where the weighings were made, and the suspension connected to the arm of the balance. A certain time was allowed for the ice to assume the temperature of the air in the vessel, which was not long because the temperature of the ice was nearly, if not always, zero when introduced. A slight evaporation from the ice was noticed when thus suspended, by its growing steadily lighter, but this never amounted to more than a milligram on the total weight of about 250 grams, during the time. As soon as the weight was accurately determined, the ice water was allowed to run in and fill the vessel. The loss in weight was then determined by the new weighing. Should the ice have been colder than the water, so as to have increased at the expense of the water in contact with it, the weight would not have been constant, but would

have steadily diminished. On the other hand, if the water was not at zero but had been slightly above, some ice would have been melted and the weight steadily increased. As a matter of fact this happened after an immersion of about half an hour, but during the first twenty minutes remained very constant.

For a second measurement, the vessel was removed from the mixture, emptied and carefully dried inside. The ice being also removed, the suspension was dried and weighed.

Careful determinations had to be made of the density of the water used in the snow mixture, which was the river water supplied to the college mains. This, during the winter months, was very clear and quite pure. The observations were made on water emptied from the vessel after a measurement.

The following table gives the result of seven determinations which we made by this method for the different pieces of ice:

ON THE DENSITY OF ICE. METHOD OF WEIGHING IN WATER AT 0° C.

Date.	Year of Formation.	Density.	Difference from Mean.
March 9th.	1901	.91684	.00023
" "	1901	.91665	.00004
" "	1900	.91661	.00000
" 16th.	1900	.91642	.00019
" "	1899	.91650	.00011
" "	1899	.91648	.00013
" 23d.	1900	.91678	.00017

Mean = .916611 ± .000065.

The deviations are not larger than would have been obtained by other methods, and may be ascribed partly to variations in the density of the different pieces. We think that a check of the accuracy of the method is afforded by the two determinations of 1899 ice, the second measurement being made with the same piece of ice. This was done by removing the piece after the first measurement, drying it carefully outside in the cold air and repeating the observations. The two determinations thus obtained are .91650 and .91648. All the other measurements were for different pieces varying in size.

The mean value obtained is somewhat lower than the result given by Nichols for river ice, and higher than given by him for artificial ice, but agrees well with his measurements for old river ice.

It is evident that, according to the present determinations, the density of old and new river ice is the same. It appears that the density of the clear river ice may be taken as

$$.91661 \pm .00007$$

which agrees to two parts in 10,000 with the value given by Nichols for natural river ice not newly cut, which is .91644, and to the same order of accuracy with the measurements of Bunsen.

McGILL UNIVERSITY, April 27, 1901.

NOTE.

Henry Augustus Rowland, Physicist.—Professor Rowland was born at Honesdale, Pa., on November 27, 1848. He studied civil engineering at the Rensselaer Polytechnic Institute where he received his first degree in 1870. After two years, spent partly in the field as a surveyor and partly in teaching at Wooster College, Ohio, he returned to Troy as instructor in physics. In 1874, he was promoted to an assistant professorship.

In 1875 Rowland, whose extraordinary gifts were becoming known, was offered a place in the newly organized faculty of the Johns Hopkins University, and after a year abroad, a portion of which was spent in the laboratory of von Helmholtz, he entered upon his duties at Baltimore as head of the department of physics, which position he held until his death on April 16, 1901. Although his stay in Berlin was brief, the greater part of his year abroad being devoted to visiting the great centers of scientific activity and in collecting apparatus for his new laboratory, he found time to carry to completion a very important research on the Magnetic Action of a Moving Electrostatic Charge. The impression made upon his coworkers in the laboratory by this piece of work was a profound one, not less on account of the fundamental character of the experiment than of the extraordinary quickness with which the definitive result was reached. Such celerity of performance was quite beyond the experience of the German investigators who were accustomed to devote months and years to the establishment and verification of their results; but although there was much doubtful shaking of heads over the restless haste of the young American, his power as an investigator was fully recognized by the eminent director of the laboratory,[1] who paid Rowland the then very unusual compliment of making his work the subject of an immediate report to the Berlin Academy of Sciences.

The subsequent history of this research is an interesting one. Lecher[2] in 1884 repeated the experiment with seemingly unimportant modifications, but obtained wholly a negative result. Roentgen[3] in 1888 confirmed the existence of the effect. The following year, Rowland, in collaboration with Hutchinson, attacked the problem again with much

[1] Helmholtz: Berl. Berichte, 1876.
[2] Lecher: Rep. der Physik, XX., p. 151, 1884.
[3] Roentgen: Berl. Berichte, Jan. 19, 1888, p. 23.

more elaborate apparatus. They not only reëstablished the existence of the phenomenon to their own satisfaction, but were able to show that the observed results were in fair agreement with the computed values and with those obtained in the original experiment.[1] Himstedt[2] simultaneously and independently made measurements with an apparatus essentially similar to that of Rowland and Hutchinson. He likewise found an easily measurable effect; indeed his instrument was of sufficient sensitiveness in some instances to give deflections of more than 100 scale divisions. Himstedt hints that the failure of Lecher to obtain a positive result was probably due to a lack of sensitiveness in his apparatus. This seems hardly probable, since Lecher used an astatic needle in the axis of a vertical disk 200 centimeters in diameter, charged to 5,000 volts and driven at the rate of 200 revolutions per second. The charge was measured by means of an absolute electrometer. In 1889 Lippmann[3] called attention to the reciprocal of the Rowland effect and showed that variations in a magnetic field ought to produce a movement of electrified bodies placed therein. In 1897 Cremieu,[4] at his suggestion, undertook to test this conclusion experimentally by means of an apparatus with which he was led to expect, in accordance with his computations, an effect amounting to about one-thousandth of a dyne. He, however, obtained a purely negative result. In subsequent experiments[5] he obtained no deflection where the computed effect should have been 140 millimeters. A repetition of the original experiment with apparatus essentially similar to that employed by Rowland, and Hutchinson and by Himstedt likewise gave no deflection although the computed effect was 175 millimeters. Cremieu considers that he has discovered the source of the discrepancy between his results and those of his predecessors. He argues that the effects obtained with the earlier forms of apparatus are not due directly to the magnetic action of the moving electric charge, but to a rapid succession of instantaneous currents set up in the intervening sectors of metal under the action of the charged sectors of the moving disk.

In the fall of 1900 Professor Rowland returned for the second time to the attack of this problem and he had the satisfaction before his death of seeing his original conclusions reaffirmed at the hands of one of his own students. The singular conflict of evidence was indeed of a sort that could scarcely be settled without further experimental work, for as Rowland had himself pointed out in a brief letter to the editors of the *Philosophical Magazine*,[6] in which in vigorous and characteristic language

[1] Philosophical Magazine, 5, XXVII., p. 445, 1889.
[2] Wiedemann's Annalen, 38, p. 560, 1889.
[3] Lippmann: Comptes Rendus, 89, p. 151, 1889.
[4] Cremieu: Comptes Rendus, 130, p. 1544, 1900.
[5] Comptes Rendus, 131, pp. 578–797.
[6] Philosophical Magazine (3), viii, p. 442.

he insisted upon his rights as the originator of every detail of the experiments described in the communication to the Berlin Academy in 1876, Helmholtz had before that time looked for the effect without result so that it was a question of Rowland and his coworkers and Himstedt, versus Helmholtz, Lecher and Cremieu.

In this piece of work Rowland exhibited many of the qualities that have characterized his entire scientific career. His power of discriminating between the truly fundamental and important aspects of science and those which are secondary was no less remarkable than the directness of his method of attack, and these qualities were combined with three others which are equally important to the investigator; mathematical skill, mechanical insight and a wonderfully clear conception of what he regarded as the *modus operandi* of nature. His knowledge of machinery appears to have been instinctive rather than acquired and this was the quality of mind upon which he seems chiefly to have prided himself. Of his no less remarkable mathematical power he professed to have a poor opinion; but he said that he had never seen a machine every detail in the working of which he could follow with ease. His views concerning molecular mechanics and the mechanism of the ether were those of Faraday and Maxwell, and it is possibly because of the fixity of his conviction of the correctness of the Maxwellian conception that he took no part in the modifications and development of that great theory which has of recent years taken place at the hands of Hertz, Boltzmann, Lorentz, Planck and others.

It is in the realm of the definite rather than in the semi-speculative region beyond the boundary of the tangible that Rowland's contributions to science lie. He selected by preference problems the solutions of which must consist of precise quantitative results obtained by means of measurements with perfectly designed and accurately constructed apparatus, and in such work he had no superior. The clearness with which he saw the essential conditions of a problem and the completeness with which he succeeded in fulfilling them secured for his methods immediate and universal recognition and caused his results to be received as standards.

In his earliest publication of importance, in 1873, Rowland applied, for the first time, the analogue of Ohm's law to the magnetic circuit and laid the foundations of the precise study of magnetic permeability. Almost immediately upon his return from Europe he began his classical measurement of the mechanical equivalent of heat. The memoir describing these experiments, which was published in 1880 in the Proceedings of the American Academy, stands almost alone in completeness and precision and for the thoroughness with which every source of error was studied and accounted for. His values of Joule's equivalent have stood

the severe test of comparison with all the more recent determinations and the slight discrepancy which for a time appeared to exist between them and the values obtained by electrical methods has recently been completely accounted for and eliminated by redeterminations of the electromotive force of the Clark cell at the hands of Jaeger, Kahle and of Carhart and Guthe. His determination of the variation of the specific heat of water with the temperature has likewise received substantial confirmation in the recent work of Barnes.

To the important subject of the determination of the value of the ohm, Rowland began to turn his attention soon after the opening of the Johns Hopkins Laboratory and measurements by modifications of the methods of Kirchhoff and of Lorenz were continued at his hand and under his direction at the hands of Kimball, Duncan, Wilkes and Hutchinson for a period of twelve years. In the meantime a variety of lesser topics such as the electric absorption of crystals, the diamagnetic constants of bismuth and calcite and the phenomenon discovered by E. H. Hall and subsequently known as the Hall effect received consideration. To the same period belongs the beginning of his greatest scientific achievement; the production of the concave diffraction grating and its application in the study of the spectrum.

In this work the genius of Rowland had ample scope; the investigation demanded theoretical insight, the ability to design machinery for the ruling of gratings of unapproachable perfection and an extraordinary degree of patience and skill in the use of them when made. The skill and intelligence of others was extensively drawn upon, but the central figure throughout the prolonged and arduous task was always that of Rowland. He invented the method of producing an approximately perfect screw and devised the method of eliminating its errors. The grinding of a perfect surface upon which to make the rulings called out the supreme skill of Brashear; but the idea of ruling upon the face of a concave mirror was Rowland's and he it was who better than any one else could set the diamond to produce the desired quality of line. The operation of the dividing engines was for many years the chief occupation of the mechanician Schneider who brought to this arduous labor almost infinite delicacy and patience; but the perfect system of temperature control, essential to the production of satisfactory gratings was due to Rowland and it was to his exacting scrutiny that every product of the machine was ultimately submitted.

In the long series of investigations made with gratings in the Johns Hopkins Laboratory, Rowland was assisted by Bell, Ames, Crew, Humphreys, Jewell and many others. The photographic mapping of the solar spectrum and of the arc spectra of metals occupied many years and a vast amount of data was collected, only a portion of which has as yet been published.

It is noteworthy that these greater researches were not taken up one after the other, each claiming the investigator's attention for a brief period, to be put aside as completed and replaced by another, but that they all appear to have had their origin at about the same time (in the period 1876–1881) and to have been carried simultaneously in mind for many years.

Outwardly Rowland's personality was a striking one. He was tall and erect, with a certain severity of countenance which betokened a high standard of performance and impatience of mediocrity, and with a directness and intensity of gaze that matched his extreme frankness of speech. He was fond of outdoor recreation, was an expert fisherman and sailor and a daring cross-country horseman.

For elementary routine teaching he had neither taste nor aptitude and even of the more advanced students only those who were able to brook severe and searching criticism reaped the full benefit of being under him; but he contributed that which in a university is above all teaching of routine, the spectacle of scientific work thoroughly done and the example of a lofty ideal.

That Rowland possessed the qualities of a great inventor, as well as of a man of science must be obvious to all who know his work. When in his later years he turned to engineering problems and to electrical inventing, it seemed to many that he was departing widely from the principles of his own fine *plea for pure science*, uttered in the American Association address of 1883; but when in 1899, as first president of the American Physical Society, he spoke again, and, as it proved, for the last time upon a general theme, it was in the same high and inspiring tone as of old.

The recognition of Rowland's genius was early and universal. He was honored by election to nearly all the important scientific bodies abroad and received numerous prizes and medals abroad and at home. In 1881, when he was only 33 years of age, he became a member of the National Academy of Sciences, the youngest man probably upon whom that honor had ever been conferred.

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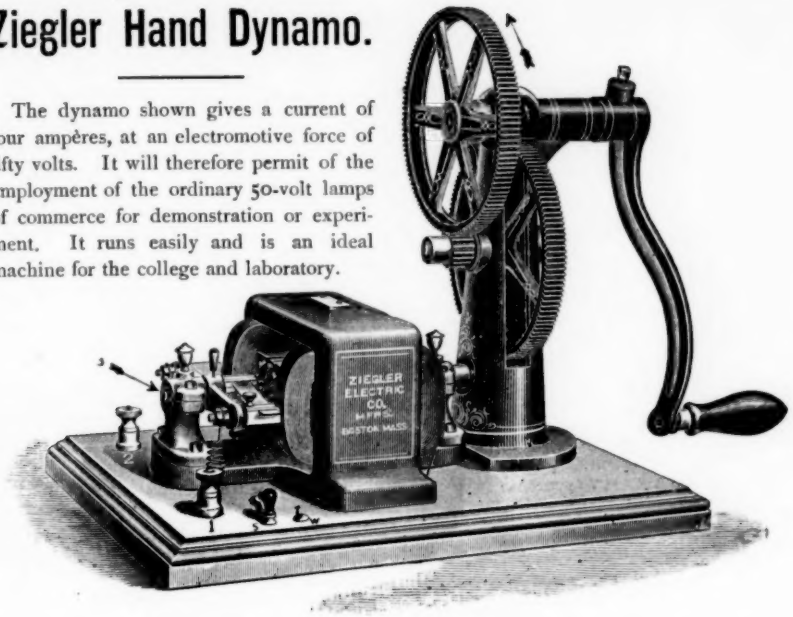

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THE PHYSICAL REVIEW

A Journal of Experimental and Theoretical Physics

CONDUCTED BY

EDWARD L. NICHOLS, ERNEST MERRITT and FREDERICK BEDELL

LXIII. May, 1901

TABLE OF CONTENTS

Condensation

Surface Tension at the Interface of Two Liquids Determined Experimentally by the Method of Ripple Waves. FLOYD R. WATSON.

An Improved Method of Eating Shelled Pecan. JOHN O. REED.

George Francis Fitzgerald. J. LARMOR.

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LXIV. June, 1901

TABLE OF CONTENTS

The Influence of Temperature upon the Photo-electric Effect. JOHN ZELENY.

Currents and Potential on Submarine Cables produced by Sine-wave Electromotive Forces. A. C. CREHORE.

The Two Gaseous Heats of Gases. W. P. BOYNTON.

On a Form of Artificial Submarine Cable. AUGUSTUS TROWBRIDGE.

Force Due to "Continuous Impact." FREDERICK SLATE.

The Wilder Physical Laboratory of Dartmouth College. E. F. NICHOLS.

On a Method for the Determination of the Critical Velocity of Fluids. H. T. BARNES and E. G. COKER.

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PUBLISHED FOR CORNELL UNIVERSITY

THE MACMILLAN COMPANY